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REGISTERED No. M. 3121

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XIII] *SECTION A* [No. 1

JANUARY, 1941

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, HEBBAL, BANGALORE.

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v. 13, no. 1-6

CRYSTALS AND PHOTONS*

By Sir C. V. Raman

My first duty on this occasion is to express our gratitude to the authorities of the Andhra University for their generous sympathy and support to the work of the Academy and the opportunity they have afforded us of having our Annual Meeting in a truly academic atmosphere set amidst the beautiful scenery of Waltair. We appreciate very much the warmth of the welcome we have received. Our gathering here gives the Fellows of the Academy an opportunity of visiting the Andhra University at a time when many new developments are receiving attention, and of meeting men like Professor Bhagavantam, Professor Seshadri and Dr. Nagendra Nath, whose research papers have filled the pages of the *Proceedings* of the Academy and whose work has shed lustre on the University. They have, like our many other Fellows in other parts of India, given ungrudgingly of their time and energy for the welfare of the Academy. Our special thanks are due to them and other local Fellows and to the Chairman and members of the Reception Committee for having worked to make this meeting a success.

In my Presidential Address last year at Bangalore, a long-term programme of research on the physics of crystals was outlined and put forward as likely to yield valuable results for our knowledge of the solid state. Looking over the *Proceedings* of the Academy for the last twelve months, I find that fourteen papers on crystal physics (listed at the end of this address) have appeared in it, of which three are from Waltair and the rest from Bangalore. We have no reason to be dissatisfied with the progress made so far, and indeed it may be claimed that some of these papers deal with the problems of the solid state from a quite novel standpoint and open up new pathways of investigation. I propose in this address to survey broadly the field of research dealt with in these papers which may be designated as the newer crystal optics based on the ideas of the quantum theory, to distinguish it from the older optics which considers the effects of passage of radiation through crystals on the wave-principles. The quantum optics links together the phenomena observed with infra-red radiation, visible light and X-rays in a remarkable way, and reveals the existence of a new type of X-ray reflection in crystals.

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* Presidential Address delivered at the Annual Meeting of the Indian Academy of Sciences held on the 27th December 1940, at the Andhra University, Waltair.

As is well known, the behaviour of a crystal with respect to common light is intimately related with the geometric symmetry of the system to which it belongs. Rock-salt and diamond, for example, which are cubic crystals are isotropic or singly refracting; calcite and sodium nitrate which are rhombohedral crystals are doubly refracting but optically uniaxial; aragonite and barite which are orthorhombic are doubly refracting but optically biaxial. These characters of the respective crystals are determined by the optical polarisability of the substance in different directions. The polarisability may be geometrically represented by a surface which is a sphere for an isotropic crystal, a spheroid of revolution for a uniaxial crystal, and an ellipsoid with three unequal axes for a biaxial crystal. The polarisability is a bulk or molar property, which is intimately connected with the atomic architecture of the crystal, that is to say, by the properties of the atoms or ions or molecules composing the crystal, and by the manner in which they are spaced, orientated and linked together. The modern techniques for growing large crystals enable us to study and exhibit the very striking optical behaviour of many common substances. Sodium nitrate, for instance, can be grown into large crystals, and a block of it shows a birefringence which is even more obvious and striking than that of calcite. Still better is naphthalene which is a biaxial crystal and shows an extremely large birefringence. *The angles of internal and external conical refraction of naphthalene are about* 14°, *and are thus eight times larger than those of aragonite with which conical refraction is usually exhibited.* Needless to say, conical refraction as observed with a piece of naphthalene is far more striking than that exhibited by aragonite. As was shown by Bhagavantam in the very first paper he published as a research student, the strong birefringence of naphthalene is closely connected with the very great optical anisotropy of the molecules as well as the special orientation of the molecules in the crystal.

The classical optics of crystals prefers to ignore the atomic architecture of the solid and regards the substance as a continuum with specific molar properties. The crystal functions as a pathway for the passage of the radiation, taking part in its propagation but remaining essentially undisturbed in the process. Even when, as frequently happens, the radiation is partially absorbed by the crystal, this is fitted mathematically into the wave-picture by making the optical constants of the substance complex quantities instead of real numbers. Such a wave-picture is a satisfactory description of the phenomena which it is intended to cover. But it is not a complete description of the facts. This was shown clearly by the studies on the scattering of light in crystals commenced by the writer in the year 1921 and culminating in the discovery of the effect of a change of frequency described in the lecture on "A New Radiation" in February 1928. The method of

observation described in that lecture involves the use of monochromatic light and a spectroscope. To take a specific example, we allow the beam of light from a mercury arc lamp to pass through a crystal of diamond. Focussing an image of the illuminated diamond on the slit of a spectroscope, we observe in the light scattered in the substance of the diamond, new lines not present in the incident radiation. Corresponding to each monochromatic line in the incident radiation, there is a second and additional line, the wave-number of which is less by 1332 per centimetre than for the incident light. A third and much feebler line of which the wave-number *exceeds* that of the incident light by 1332 per centimetre is also weakly recorded in the spectrum. Numerous such studies of the scattering of light in crystals have been made since they were first described. It is abundantly clear from the observations that they cannot be explained on the basis of the ideas of the classical wave-theory alone. It is necessary to introduce the concept of the photon or a quantum of radiation, the energy of which is proportional to the frequency of the corresponding waves. The change of frequency as actually observed appears on the quantum theory as due to an exchange of energy between the photon and the crystal, a diminution of frequency if the photon is the donor and the crystal the acceptor, and an increase if the reverse is the case.

The investigation of light scattering in crystals is a powerful method for the study of the solid state. But it is beset by peculiar experimental difficulties. Theory indicates that a perfectly homogeneous crystal would scatter no light at all; the diffusion of light theoretically possible is that due to the vibrations of the crystal lattice excited by the incident light and occurs in every case with a change of frequency. Unfortunately, however, actual crystals are far from being perfect. Internal flaws and surface imperfections result in a strong scattering of light with unaltered frequency. Theoretically this should not trouble us at all, but practically it does trouble us very much. The difficulty arises from the fact that the incident light is not truly monochromatic and usually contains additional components and some continuous spectrum. If the crystal is not clear, or if the spectrograph gives appreciable coma or scattered light of its own, there is not much hope of getting useful results. Truly monochromatic light sources, clear crystals of sufficient size with polished faces, and spectrographs of high optical perfection and illuminating power are needed for such work. When these requirements are satisfied, results of great interest and value are forthcoming.

To appreciate the significance of the results obtained in such studies, we must remember that a crystal is not a mere geometric array of atoms, molecules or ions in space, but is a coherent structure of such particles having identical properties which are held together by powerful forces, thereby

forming a rigid solid. It is inappropriate to consider the observed results in terms of the vibrations of the individual ions, atoms or molecules in a crystal. For, it is obviously not possible for any one particle in a crystal to vibrate without setting all the other particles in resonant vibration. To understand the optical behaviour of a crystal rightly, we must consider it as a whole and set ourselves to discover the various modes of vibration of which its structure is capable. These vibrations divide themselves into two classes. In the first class of vibration, we can ignore the atomic architecture of the crystal and regard it as an elastic solid traversed by acoustic waves. The frequency of such vibration may be anything from zero upwards to a value so high that the corresponding wave-length becomes comparable with the spacing of the atomic planes in the crystal. In the second class of vibration, we are dealing with movements which can only be understood or described in terms of the atomic architecture of the crystal. Such vibrations are referred to as the optical vibrations of the lattice. Some of these optical vibrations may have no counterpart at all for the substance in a fluid state and arise as a consequence of the crystal fields which bind the chemical units together into a rigid and ordered assemblage. Some of the optical vibrations, however, may have frequencies roughly corresponding to those characteristic of the ions or molecules in the fluid state. Even so, they cannot be identified with the vibrations of the individual chemical units. The optical vibrations—quite as much as the acoustic ones—are characteristic of the crystal structure and not of the individual particles present in the lattice cells.

The simplest way in which we may picture an optical vibration of a crystal lattice is to imagine the interpenetrating lattices of the simplest type present in the crystal, each carrying a single atom at the lattice points, to oscillate as rigid units relatively to each other, the centre of the inertia of the whole assembly remaining at rest. In such an oscillation, the crystal would throughout remain a homogeneous structure, but the relative positions of the atoms in its lattice cells would vary periodically with time. Such physical properties as the electric dipole moment, optical polarisabilities, and structure-amplitudes which determine the behaviour of radiation in various ranges of frequency in its passage through the crystal—would, therefore, also vary periodically with the frequency of the oscillation. It can be readily seen, however, that optical vibrations of the general description indicated would also be possible in which the phase of the oscillation changes slowly from place to place within the crystal. If this phase varies regularly in such manner as to repeat itself over a series of regularly spaced planes, the spacing of such planes is the phase wave-length of the optical vibration. An infinite phase-wave-length indicates a vibration identically the same throughout the crystal, and the optical frequency has then its limiting value.

The importance of the considerations set out above becomes clear when we consider the effect of radiations falling on a crystal. We may first refer to the case of a beam of infra-red radiation incident normally on the surface of a crystal. It is a well-known experimental fact that if the frequency of such radiation is within certain ranges characteristic of the particular substance, the radiations are powerfully reflected backwards by the crystal. This is the result of the optical vibrations of the crystal lattice being strongly excited by the incident waves. That such an excitation results in a directed reflection and not a diffuse scattering clearly indicates that the vibration of the crystal lattice is in the same phase at every point on the surface of the crystal. In the more general case of oblique incidence, in order that a regular geometric reflection may result, the excited lattice vibrations have necessarily to be coherent in phase, having everywhere the same relation to the phase of the resultant electric force due to the superposition of the incident and reflected waves. Since the waves necessarily penetrate to a certain depth, it follows that such coherence in phase must extend also into the interior of the crystal.

Passing on to the case of the scattering of light within a crystal, it is evident that an optical vibration of the crystal lattice cannot be excited by the incident light if the phase of such vibration is the same throughout the volume of the crystal. This is evident from the principle of interference, as the effects of all the secondary radiations, irrespective of their frequency, would completely cancel out. In fact, it is easy to show that a scattering of light with altered frequency within a crystal would only be possible if the lattice-vibrations have phase waves which are equally inclined to the incident and scattered waves and so spaced that the scattering is in effect a monochromatic reflection by an optically stratified medium. A very similar situation also arises when we consider the scattering of light as the result of the acoustic vibrations of the crystal lattice. The usual formula for a monochromatic reflection connects the wave-length of the incident radiation, the spacing of the optical stratifications and the glancing angle which is half the angle of scattering. This formula which follows from the classical wave-principles has its counterpart in the quantum theory, appearing as a consequence of the conservation of energy and momentum in the collision between the photon and the acoustic or optical disturbance in the crystal.

Having considered the cases of infra-red radiation, and of ordinary light, we naturally pass over to the X-ray optics of crystals. It is fairly obvious that, as in the case of ordinary light, an acoustic vibration of the lattice can only give rise to a diffuse scattering of the X-rays. The position is entirely different in regard to the optical vibrations of the crystal lattice. It follows from the very nature of an optical vibration that it does not involve any variation in the mean electronic density of a unit cell in the lattice,

but can cause only periodic variations of the structure-amplitudes of the crystal. In other words, the effect of an optical vibration is to cause a variation having its own frequency in the reflecting power of the regular crystal spacings. We may put this a little differently by stating that the optical vibration creates dynamic stratifications of electron density, and that these can give regular X-ray reflections but with a change of frequency, in much the same way as the static planes give the classical reflections without change of frequency. The spacing and orientation of the dynamic stratifications are identical with those of the static spacings when the phase-wave-length is infinite. More generally, these quantities and, therefore, also the geometric law of the modified reflection, would depend on the wave-length of the phase-waves and the angles which they make with the crystal spacings and with the plane of incidence. The geometric law of quantum X-ray reflection for the most general case has been deduced by Raman and Nath in a paper published in the *Proceedings* of the Academy for November 1940, and takes a quite simple form. It will suffice here to remark that the theory shows that the reflection should appear in precisely specifiable directions. In other words, *the spacings of a crystal should give, in addition to the classical or unmodified reflections, quantum or modified reflections obeying a different geometric law*. It is no exaggeration to remark that this new result is of the greatest importance both to X-ray optics and to crystal physics. For the experimental proof of this thesis, it is necessary that sharply defined X-ray reflections of which the positions agree with those theoretically deduced should be found in association with every crystal plane of which the structure amplitude is sufficiently large and is strongly modulated by the possible vibrations of the lattice. That this is actually the case has been demonstrated in a series of communications published during the year by Raman and Nilakantan. A specially detailed investigation for the case of diamond is appearing shortly in the *Proceedings*, which brings out in a convincing way the physical reality of the phase-waves associated with the optical vibrations of the crystal lattice. The prediction made earlier in the year that the intensity of the modified reflections given by diamond should remain unaffected at liquid air temperatures has also been completely confirmed. *The quantum theoretical character of the new reflections has thus been completely established.*

Returning to the case of the scattering of ordinary light, it may be remarked that both the acoustic and optical vibrations of the crystal lattice reveal themselves in it. The vibrations of the latter class are usually subdivided into external and internal vibrations. Though this distinction is somewhat arbitrary, it is in many cases useful; and indeed, in relation to the crystal structure, the external vibrations, the frequency of which is determined by the crystal fields and are usually much lower, are even more important

than the internal vibrations. The thermal behaviour of the external oscillations is particularly interesting. The very careful studies of the temperature effect which have been made by Nedungadi in the cases of sodium nitrate and of quartz have been very illuminating. Nedungadi's studies indicate that any transformation in crystalline form is usually *preceded* by notable changes in the magnitude and character of the low-frequency shifts. The changes observed in the case of α-quartz greatly assist in understanding the remarkable variations of physical properties which precede the α–β transformation of quartz.

The case of α-quartz has been very exhaustively investigated by Saksena with a view to identifying the various modes of optical vibrations appearing in the spectrum of the scattered light and correlating these with the known infra-red spectrum of α-quartz and with the specific heat of the crystal. The investigation must be considered to have been highly successful, as the theoretically predicted and experimentally observed behaviours show an almost complete agreement. The theoretical part of the investigation was based on an application of the methods of the group theory to the known structure of the crystal and the determination of its symmetry modes of vibration. The verification of the theoretical conclusions required an investigation of the spectra with the incident light polarised in different ways and with the crystal in different orientations, as also an analysis of the scattered light in each case. Such an investigation is naturally laborious and time-consuming, but the results in the case of quartz appear fully to have justified the trouble taken. It is very satisfactory to find from the work of Bhagavantam with calcite, and of Saksena with quartz, that the theoretical selection rules for the appearance and non-appearance of certain vibrations in the spectra are found to be obeyed. These selection rules may be deduced geometrically from the known form of the optical polarisability ellipsoid of the crystal and the character of the deformations it should undergo for vibrations of the different possible types of symmetry. The fact that the results deduced are in accord with the experimental results shows clearly that we are dealing with the vibrations of the crystal lattice and not of the individual chemical units in it, as remarked earlier in this address.

Summary

The excitation of the optical modes of vibration of a crystal lattice by radiations incident on the crystal is discussed. The optical vibrations can be described as oscillations of the interpenetrating lattices in the crystal with respect to one another. They give rise to a periodic variation of the physical constants, *e.g.*, electric dipole-moment, optical polarisabilities, structure amplitudes, which influence the behaviour of radiation in various ranges of frequency in its passage through the crystal. The phenomena observed in

the different ranges of frequency have a common feature, namely that the incident radiation excites the crystal vibrations of which the phases are everywhere in coherent relationship with the phase of the radiation field. The scattering of light or the reflection of X-rays with change of frequency appears as the result of the phase of the lattice vibrations varying from point to point in such manner that the crystal is, in effect, an optically stratified medium giving a monochromatic reflection of the incident rays at the appropriate angle of incidence determined by the spacing of the stratifications and the wave-length of the incident radiation. The description of the observed effects in the language of the wave-theory and in terms of the quantum hypothesis are complementary and do not in any way contradict each other.

The paper includes a review of 14 communications dealing with this field of research published during the year 1940 in the *Proceedings of the Indian Academy of Sciences.*

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THE SCATTERING OF CHARGED MESONS

By H. J. Bhabha, Ph.D., and B. S. Madhava Rao, D.Sc.

Received December 3, 1940

It was shown by Bhabha (1939) that the scattering of neutral mesons due to the mesic charge of the heavy particles (g_1 interaction) as given by the quantum theory has a complete correspondence with the scattering of mesons as given by the classical theory. The classical scattering is the analogue of the Thomson formula as recently extended by Dirac, remaining approximately constant up to meson energies comparable with the rest energy of the heavy particles, after which it decreases due to the effects of radiation reaction. The quantum cross-section like the Klein-Nishina formula also decreases with increasing energy due to the appearance of quantum effects, and the introduction of radiation reaction into the quantum theory would decrease it still more for high energies. On the other hand, the scattering of charged mesons on the usual theory differs completely from the classical and quantum mechanical scattering of neutral mesons, first in being larger by a factor $(M/\mu)^2$, M and μ being respectively the neutron and meson masses, and secondly in having an entirely different dependence on energy. The scattering of charged mesons due to the g_1 interaction alone was proportional to p^4/E^2, p being the momentum and E the energy of the meson. It was shown in the paper quoted above that this difference in the scattering of neutral and charged mesons is entirely due to the fact that whereas a positive meson can only be absorbed by a neutron and emitted by a proton, a neutral meson may be absorbed or emitted by either a neutron or a proton. To avoid this difference, Bhabha put forward the idea that the heavy particles might exist in states of all integral charge, positive and negative with different rest energies, of which only the two of lowest rest energy, namely the proton and neutron, occur normally in nature. This assumption puts the scattering of charged mesons due to the g_1 interaction on the same footing as the scattering of neutral mesons, and establishes correspondence with the classical theory. (*Cf.* Heitler, 1940.)

It is our purpose in this paper to investigate the modifications which the above idea of allowing the heavy particles to exist in states of all integral charge introduces in the scattering of charged mesons by the mesic dipole of the heavy particles (g_2 interaction). The dipole interaction leads even in

the classical theory to a scattering of mesons which increases with energy as p^4/E^2 in the region of low energies in which the effects of radiation reaction are negligible, and this coupled with the fact that only total scattering cross-sections have been compared, has concealed the very considerable difference in the dependence on scattering angle and polarisation of the meson which exists between the scattering on the classical theory and the usual quantum theory. It will be shown in this paper that if the heavy particles be allowed to exist in states of all integral charge, then complete correspondence is established in the scattering due to the g_2 interaction as given by the classical and quantum theories, both in its dependence on the scattering angle and on the directions of polarisation of the incident and scattered meson. This complete correspondence seems to us on the one hand to add further support to the correctness of the assumption that the heavy particles can exist in states of all integral charge, and on the other to the correctness as far as scattering phenomena are concerned of a classical theory of the spin even when applied to a particle with a spin $\hbar/2$ (with the exception of a constant numerical factor which will be discussed in detail in the last section). On the other hand the hypothesis put forward by Heitler (1940) of allowing the heavy particles to exist in states of higher spin possesses no correspondence with any classical theory. Moreover the need for it has disappeared since a complete classical theory as put forward for a Maxwell field by Bhabha (1940, *a*), and Bhabha and Corben* and for a meson field by Bhabha* (1940, *c*) has shown that the effect of radiation reaction is ultimately to make the scattering due to the spin diminish as E^{-2} instead of increasing as E^2.

Quantum Mechanical Scattering

We will first consider the scattering of charged mesons due to the g_2 interaction on the basis of the assumption that the heavy particles can exist in states of all integral charge positive and negative with different rest masses (Bhabha, 1940, *b*). Neglect the mass difference between a proton and a neutron, and in the notation of the above paper let $\triangle M_2$ and $\triangle M_{-1}$, denote the mass excesses of protons of charge $2e$ and $-e$ respectively over that of an ordinary proton. Since we are interested in investigating the effect of the above assumption on the scattering by the spin, we put $g_1 = 0$. For the same reason we will put $M = \infty$ as has been done in the classical calculations. This is equivalent to treating the heavy particles as fixed in space. The correction due to the motion of the heavy particles is of the order $(\mu/M)^2$

* *Proc. Roy. Soc.* (A), in print.

for the case of low momenta $p \ll Mc$ to which we restrict ourselves, and is hence negligible.

In this paper we adopt the notation used by Bhabha (1938) in the formulation of meson theory. $\mathbf{p}$ denotes the momentum of a meson, and $E = c\sqrt{\mu^2 c^2 + p^2}$, its energy. ϵ_{1p}, ϵ_{2p} and ϵ_{3p} are three mutually perpendicular unit vectors, ϵ_{3p} being in the direction $\mathbf{p}$. As usual α, β denote the four Dirac matrices, and we define a_{1p}, a_{2p}, a_{3p} as in the above paper by

$$\left.\begin{aligned} a_{1p} &= (\alpha, \epsilon_{1p}) \\ a_{2p} &= (\alpha, \epsilon_{2p}) \\ a_{3p} &= (\alpha, \epsilon_{3p}) = (\alpha, \mathbf{p})/p \end{aligned}\right\} \tag{1}$$

Since the mass of the heavy particles is treated as infinite, we may proceed as in the usual non-relativistic approximation and replace products of two α's, by the Pauli matrices σ_k, σ_l, σ_m, thus

$$\sigma_k \sigma_l = i\sigma_m. \tag{2}$$

In this approximation $\beta = -1$ and terms containing an odd number of α's are negligible. Using (1) and (2)

$$\left.\begin{aligned} (a_{3p}\, a_{1p}) &= i(\sigma, \epsilon_{2p}) = i\sigma_{2p} \\ (a_{3p}\, a_{2p}) &= -i(\sigma, \epsilon_{1p}) = -i\sigma_{1p} \end{aligned}\right\} \tag{3}$$

The interaction of mesons with the heavy particles is given by $\mathcal{J}_0$ in the paper mentioned above (formula 58 *a*). τ_{NP} and τ_{PN} are there the operators which convert a proton into a neutron and *vice versa*. On the basis of the new idea, we have to replace these as in the previous paper (Bhabha, 1940, *b*) by τ_- and τ_+ which respectively decrease and increase the charge of the heavy particles by one unit. Putting $g_1 = 0$, and remembering (3), the interaction of mesons with the heavy particles in the non-relativistic approximation of this paper is then

$$\mathcal{J}_0 = -\frac{g'^2}{\sqrt{2EV}} \sum_p \frac{p}{\mu c} \left[\left\{\sigma_{2p}\,(\bar{a}_{1p} - b_{1p}) - \sigma_{1p}\,(\bar{a}_{2p} - b_{2p})\right\} \tau_- e^{-\frac{i}{\hbar}(\mathbf{p}, \mathbf{X})}\right.$$

$$\left. + \left\{\sigma_{2p}\,(a_{1p} - \bar{b}_{1p}) - \sigma_{1p}\,(a_{2p} - \bar{b}_{2p})\right\} \tau_+ e^{\frac{i}{\hbar}(\mathbf{p}, \mathbf{X})}\right] \tag{4}$$

As usual $g'_2 = g_2 \mu c/\hbar$. Here V is the volume of some very large box in which the wave functions are assumed to be periodic and at the end of the calculation V is made to tend to infinity. $\bar{a}_{1p}$ and a_{1p} are the operators which give the creation and annihilation of positive mesons of momentum $\mathbf{p}$ polarised in the direction ϵ_{1p}, and $\bar{b}_{1p}$ and b_{1p} are the corresponding operators for negative mesons. $\mathbf{X}$ represents the co-ordinates of the heavy particles.

Now consider the scattering of a negative meson of momentum $\mathbf{p}$ by a proton. The momentum of the scattered meson will be denoted by $\mathbf{p}'$. Denote the angle between $\mathbf{p}$ and $\mathbf{p}'$ by θ. It can be shown as usual that the differential cross-section dQ for the scattering of the meson into the solid angle $d\Omega$ is given by

$$dQ = 4E^2 V^2 \left| \sum_m \frac{(i|\, \mathcal{J}_0 |\, m)\,(m|\, \mathcal{J}_0 |\, f)}{E_i - E_m} \right|^2 d\Omega \qquad (5)$$

where i, m and f denote the initial, intermediate, and final states of the whole system, E_i and E_m being the total energies of the initial and intermediate states of the whole system. There are four intermediate states m by which the process takes place.

$$U^- + P + [N] + [P_2] \rightarrow \left\{ \begin{array}{c} N + [N] + [P_2] \\ \hline U^- + P + U'^- + P' + [P_2] \\ \hline U^- + P_2 + U'^- + [N] + [P_2] \\ \hline P + [N] + P' \end{array} \right\} \rightarrow U'^- + P' + [N] + [P_2] \quad (6)$$

The square brackets denote a virtual neutron and a proton of charge $2e$ in their negative energy states. For the four intermediate states, $(E_i - E_m)$ is respectively E, $(-2M - E)$, $(-E - \Delta Mc^2)$, and $(-2M - \Delta Mc^2 + E)$, where for brevity we write ΔM in place of ΔM_2. Since M is taken as infinite, the second and fourth intermediate states give no scattering and the scattering comes only from the first and third intermediate states. On the old theory there would be no intermediate state like the third.

Take the vectors ϵ_{2p}, $\epsilon_{2p'}$ to lie in the $\mathbf{p}$, $\mathbf{p}'$ plane. Then $\epsilon_{1p} = \epsilon_{1p'}$ are perpendicular to this plane. There are four cases to be considered depending on the polarisation of the incident and scattered meson. The case in which the meson is initially polarised in the direction ϵ_{2p}, the scattered meson being polarised in the direction $\epsilon_{2p'}$ we denote schematically by $(2p) \rightarrow (2p')$. The other three cases are $(2p) \rightarrow (1p')$, $(1p) \rightarrow (2p')$ and $(1p) \rightarrow (1p')$. We notice at once that the interaction (4) does not involve longitudinally polarised mesons, *i.e.*, those polarised along ϵ_{3p}. These are therefore not scattered at all by the spin of the heavy particles in the non-relativistic approximation.

Denote the two possible spin states of the heavy particles by

$$a_{\mathrm{I}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$
$$a_{\mathrm{II}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \qquad (7)$$

First consider the case $(2\,p)\rightarrow(2\,p')$. For the transition *via* the first intermediate state in (6) we get, using (4)

$$\frac{(i\,|\,\mathfrak{H}_0|\,m)\,(m|\,\mathfrak{H}_0\,|\,f)}{\mathrm{E}_i-\mathrm{E}_m}=\frac{g'^{\,2}_2}{2\mathrm{E}^2\,\mathrm{V}}\cdot\frac{p^2}{\mu^2\,c^2}\sum_{m=\mathrm{I,\,II}}(\bar{a}_f\,\sigma_{1p'}\,a_m)\,(\bar{a}_m\,\sigma_{1p}\,a_i)\cdot$$

The summation over the two spin orientations of the intermediate state can be carried out at once, and gives the unit matrix 1, thus

$$\sum_{m=\mathrm{I,\,II}}(\bar{a}_f\,\sigma_{1p'}\,a_m)\,(\bar{a}_m\,\sigma_{1p}\,a_i)=(a_f\,\sigma_{1p'}\,1\,\sigma_{1p}\,a_i)=(a_f\,\sigma_{1p'}\,\sigma_{1p}\,a_i),$$

whence

$$\frac{(i|\,\mathfrak{H}_0\,|\,m)\,(m\,|\,\mathfrak{H}_0\,|\,f)}{\mathrm{E}_i-\mathrm{E}_m}=\frac{g'^{\,2}_2}{2\,\mathrm{E}\,\mathrm{V}}\cdot\frac{p^2}{\mu^2\,c^2}\,\frac{(a_f\,\sigma_{1p'}\,\sigma_{1p}\,a_i)}{\mathrm{E}}\cdot\tag{8}$$

The transition *via* the third intermediate state similarly gives

$$\frac{(i\,|\,\mathfrak{H}_0\,|\,m)\,(m\,|\,\mathfrak{H}_0|\,f)}{\mathrm{E}_i-\mathrm{E}_m}=\frac{g'^{\,2}_2}{2\,\mathrm{E}\,\mathrm{V}}\cdot\frac{p^2}{\mu^2\,c^2}\cdot\frac{(a_f\,\sigma_{1p}\,\sigma_{1p'}\,a_i)}{-\mathrm{E}-\Delta\mathrm{M}c^2}\tag{9}$$

Thus, substituting (8) and (9) into (5), the differential cross-section for the transition $(2\,p)\rightarrow(2\,p')$ is

$$d\mathrm{Q}\,\{(2p)\rightarrow(2p')\}=\frac{g'^{\,4}_2\,p^4}{\mu^4\,c^4}\left|\frac{(a_f\,\sigma_{1p'}\,\sigma_{1p}\,a_i)}{\mathrm{E}}-\frac{(a_f\,\sigma_{1p}\,\sigma_{1p'}\,a_i)}{\mathrm{E}+\Delta\mathrm{M}c^2}\right|^2 d\Omega\tag{10}$$

The summation over the two final spin states of the heavy particle and the averaging over the two initial spin states can be carried out as usual and we get

$$\begin{aligned}&\tfrac{1}{2}\sum_{f=\mathrm{I,\,II}}\;\sum_{i=\mathrm{I,\,II}}\left|\frac{(a_f\,\sigma_{1p'}\,\sigma_{1p}\,a_i)}{\mathrm{E}}-\frac{(a_f\,\sigma_{1p}\,\sigma_{1p'}\,a_i)}{\mathrm{E}+\Delta\mathrm{M}c^2}\right|^2\\&=\tfrac{1}{2}\,\mathrm{Spur}\left[\frac{\sigma_{1p}\,\sigma_{1p'}\,\sigma_{1p'}\,\sigma_{1p}}{\mathrm{E}^2}+\frac{\sigma_{1p'}\,\sigma_{1p}\,\sigma_{1p}\,\sigma_{1p'}}{(\mathrm{E}+\Delta\mathrm{M}c^2)^2}-2\,\frac{\sigma_{1p'}\,\sigma_{1p}\,\sigma_{1p'}\,\sigma_{1p}}{\mathrm{E}\,(\mathrm{E}+\Delta\mathrm{M}c^2)}\right]\\&=\left[\frac{1}{\mathrm{E}^2}+\frac{1}{(\mathrm{E}+\Delta\mathrm{M}c^2)^2}-\mathrm{Spur}\,\frac{\sigma_{1p'}\,\sigma_{1p}\,\sigma_{1p'}\,\sigma_{1p}}{\mathrm{E}\,(\mathrm{E}+\Delta\mathrm{M}c^2)}\right]\end{aligned}\tag{11}$$

It can easily be shown that if $\mathbf{k}$ and $\mathbf{l}$ be any two vectors

$$\mathrm{Spur}\,(\sigma\mathbf{k})\,(\sigma\mathbf{l})\,(\sigma\mathbf{k})\,(\sigma\mathbf{l})=4\,(\mathbf{k}\,\mathbf{l})^2-2k^2\,l^2\tag{12}$$

Applying this formula to the spur in (11) and remembering that ϵ_{1p} and $\epsilon_{1p'}$ lie in the same direction we get

$$d\mathrm{Q}\,\{(2p)\rightarrow(2p')\}=g'^{\,4}_2\,\frac{p^4}{\mu^4\,c^4}\left[\frac{1}{\mathrm{E}^2}+\frac{1}{(\mathrm{E}+\Delta\mathrm{M}c^2)^2}-\frac{2}{\mathrm{E}\,(\mathrm{E}+\Delta\mathrm{M}c^2)}\right]d\Omega\;(13\,a).$$

Now $\Delta\mathrm{M}c^2$ lies between 15 and 20 M.e.V. (*cf.* Heitler, 1940), while E must be greater than $\mu\,c^2\approx 85$ M.e.V., the rest energy of a meson. Hence $\Delta\mathrm{M}c^2/\mathrm{E}$

is less than or of the order 1/5. To a rough approximation we may expand (13 *a*) in powers of $(\Delta Mc^2/E)$ and get

$$dQ\{(2p)\rightarrow(2p')\} = g'^4_2 \frac{p^4}{\mu^4 c^4 E^2}\left\{\left(\frac{\Delta Mc^2}{E}\right)^2 - 2\left(\frac{\Delta Mc^2}{E}\right)^3 + \cdots\right\}d\Omega \quad (13\,b)$$

Now consider the transition $(2p)\rightarrow(1p')$. The cross-section for this is just got by replacing $\sigma_{1p'}$ in formulæ (10) and (11) by $\sigma_{2p'}$. Using (12) and remembering that $\epsilon_{2p'}$ and ϵ_{1p} are perpendicular, we get

$$dQ\{(2p)\rightarrow(1p')\} = g'^4_2 \frac{p^4}{\mu^4 c^4}\left[\frac{1}{E^2} + \frac{1}{(E+\Delta Mc^2)^2} + \frac{2}{E(E+\Delta Mc^2)}\right]d\Omega \quad (14\,a)$$

$$\approx 4\,g'^4_2 \frac{p^4}{\mu^4 c^4 E^2}\left\{1 - \left(\frac{\Delta Mc^2}{E}\right) + \frac{5}{4}\left(\frac{\Delta Mc^2}{E}\right)^2 - \cdots\right\}d\Omega \quad (14\,b)$$

Next consider the transition $(1p)\rightarrow(2p')$. We have now to replace σ_{1p} in (10) and (11) by σ_{2p}. Since ϵ_{2p} and $\epsilon_{1p'}$ are perpendicular, we get as before

$$dQ\{(1p)\rightarrow(2p')\} = g'^4_2 \frac{p^4}{\mu^4 c^4}\left[\frac{1}{E^2} + \frac{1}{(E+\Delta Mc^2)^2} + \frac{2}{E(E+\Delta Mc^2)}\right]d\Omega \quad (15)$$

Finally for the transition $(1p)\rightarrow(1p')$ we have to replace σ_{1p} and $\sigma_{1p'}$, in (10) and (11) by σ_{2p} and $\sigma_{2p'}$ respectively. Using (12) and remembering that ϵ_{2p}, $\epsilon_{2p'}$, both lie in the $\mathbf{p}\,\mathbf{p}'$ plane and that the angle between them is in consequence the scattering angle θ, so that Spur $(\sigma_{2p}\,\sigma_{2p'}\,\sigma_{2p}\,\sigma_{2p'}) = 4\cos^2\theta - 2$ we get

$$dQ\{(1p)\rightarrow(1p')\} = g'^4_2 \frac{p^4}{\mu^4 c^4}\left[\frac{1}{E^2} + \frac{1}{(E+\Delta Mc^2)^2} - \frac{2\cos 2\theta}{E(E+\Delta Mc^2)}\right]d\Omega \quad (16\,a)$$

$$\approx 4g'^4_2 \frac{p^4}{\mu^4 c^4 E^2}\sin^2\theta\left\{1 - \left(\frac{\Delta Mc^2}{E}\right) + \left(\frac{\Delta Mc^2}{E}\right)^2\left(1 + \frac{1}{4}\operatorname{cosec}^2\theta\right) - \cdots\right\}d\Omega \quad (16\,b)$$

Adding (13), (14), (15), and (16), and dividing by 2 we find that the differential cross-section for the scattering of a meson through an angle θ, averaged over the two directions of transverse polarisation of the incident meson is

$$dQ = 2g'^4_2 \frac{p^4}{\mu^4 c^4}\left[\frac{1}{E^2} + \frac{1}{(E+\Delta Mc^2)^2} + \frac{\sin^2\theta}{E(E+\Delta Mc^2)}\right]d\Omega \quad (17)$$

The total cross-section is then

$$Q = 8\pi \frac{g'^4_2 p^4}{\mu^4 c^4}\left[\frac{1}{E^2} + \frac{1}{(E+\Delta Mc^2)^2} + \frac{2}{3}\frac{1}{E(E+\Delta Mc^2)}\right] \quad (18\,a)$$

$$\approx \frac{64\pi}{3}\frac{g'^4_2 p^4}{\mu^4 c^4 E^2}\left\{1 - \left(\frac{\Delta Mc^2}{E}\right) + \frac{11}{8}\left(\frac{\Delta Mc^2}{E}\right)^2 - \cdots\right\} \quad (18\,b)$$

To get the scattering of neutral mesons we remember that when a neutral meson is emitted or absorbed, a proton remains a proton and a neutron a neutron. The calculation is exactly the same, and the cross-sections for the scattering of neutral mesons in the four cases considered above are given by formulæ (13) to (16) if we put $\Delta Mc^2 = 0$ in them. Thus the total scattering cross-section for neutral mesons is got by putting $\Delta Mc^2 = 0$ in (18) and is

$$Q \text{ (neutral)} = \frac{64\pi}{3} \frac{g'^4 p^4}{\mu^4 c^4 E^2}. \tag{19}$$

As stated before, the scattering process on the old theory of charged mesons took place *via* the first intermediate state in (6) only. Hence, on the old theory the second term in (10) would be absent. As a result, the last two terms in (11) would drop out, and the scattering cross-section for each of the four cases considered above would be just

$$dQ \text{ (old theory)} = \frac{g'^4 p^4}{\mu^4 c^4 E^2} d\Omega. \tag{20}$$

Classical Scattering

The general classical theory of the scattering of mesons by spinning particles taking radiation reaction into account has been given by Bhabha in a recent paper* (1940, *c*). For low energies the effects of radiation reaction are negligible, and it is only in this region that the classical and quantum theories can be compared. In this paper, therefore, we will neglect the terms expressing the effects of radiation reaction in the formulæ given in the paper mentioned. We will follow the notation of this paper except for one minor alteration.

In the classical theory neither μ nor $\hbar$ appear separately, but only in the combination $\chi = \mu c/\hbar$. As in A, we consider the scattering of a meson wave of frequency $c\omega_0$ with a magnetic force $\mathbf{H}$ perpendicular to the direction of propagation.

As before, the heavy particle which does the scattering is taken as fixed ($M = \infty$) and its spin is represented by a unit vector $\mathbf{M}$. The angular momentum of the spin is denoted by I. The magneto-mesic force acting on the spin due to the incident meson wave can be written in the form

$$\mathbf{H} = \mathbf{H}_0 \cos c\omega_0 t \tag{21}$$

* *Proc. Roy. Soc.* (A), in print—referred to here as A.

where $\mathbf{H}_0$ is a constant. The average rate of flow of energy in the incident wave is then

$$\frac{\mathrm{H}_0^2}{8\pi} \frac{c\omega_0}{(\omega_0^2 - \chi^2)^{\frac{1}{2}}}. \tag{22}$$

The scattering will be calculated for small oscillations of the dipole, and corresponding to (21) we write

$$\mathbf{M} = \mathbf{M}_0 + \mathbf{M}_1 \sin c\omega_0 t \tag{23}$$

where $\mathbf{M}_0$ is the initial direction of the dipole, $\mathbf{M}_0^2 = 1$, and $\mathbf{M}_1$ is a direction perpendicular to $\mathbf{M}_0$, that is $(\mathbf{M}_0\ \mathbf{M}_1) = 0$. Denote the angle* between $\mathbf{M}_0$ and $\mathbf{H}_0$ by ϕ. (23) is the expression to which the oscillation of the dipole given in A reduces if radiation reaction be neglected. Then as shown in A,

$$|\mathrm{M}_1| = \frac{g_2 \mathrm{H}_0 \sin\phi}{\mathrm{I}\, c\omega_0} \tag{24}$$

and $\mathbf{M}_1$ lies in the direction $[\mathbf{M}_0 \times \mathbf{H}_0]$, so that $(\mathbf{M}_1\ \mathbf{H}_0) = 0$.

The potentials at a large distance $\mathbf{r}$ due to a vibration of the dipole given by (23) are

$$\left.\begin{aligned} \mathrm{U}_0^{ret} &= 0 \\ \mathbf{U}^{ret} &= \frac{g_2 (\omega_0^2 - \chi^2)^{\frac{1}{2}}}{r^2} [\mathbf{r} \times \mathbf{M}_1] \cos\{c\omega_0 t - r\sqrt{\omega_0^2 - \chi^2}\} \end{aligned}\right\} \tag{25}$$

Put the dipole at the origin of co-ordinates and take the z-axis along the direction of the incident meson wave. This is the direction of the vector $\mathbf{p}$ of the last section. Choose the y-axis so that the direction $\mathbf{r}$ lies in the y-z plane and as in the last section denote the angle which $\mathbf{r}$ makes with the z-axis by θ. The direction $\mathbf{r}$ is the direction of the scattered wave $\mathbf{p}'$ of the last section.

(25) shows that the potential $\mathbf{U}$ is perpendicular to $\mathbf{r}$, so that the scattered wave is always transverse. Further, a longitudinally polarised wave has no magneto-mesic force $\mathbf{H}$, so that no scattering of longitudinally polarised waves by the dipole takes place. We have then only to calculate the dependence of the scattering on the two transverse directions of polarisation of the incident and scattered waves.

First consider the case $(2p) \rightarrow (2p')$. Here the potential of the incident wave is along the y-axis, so that $\mathbf{H}_0$ must lie along the negative x-axis. Then

* This angle was called θ in A, but since θ has been used to denote the scattering angle in this paper, we have changed its symbol to ϕ.

since $\mathbf{M}_1$ is perpendicular to $\mathbf{H}_0$, it lies in the y-z plane, and hence $[\mathbf{r} \times \mathbf{M}_1]$ in (25) is perpendicular to the y-z plane. Thus the scattered wave has no component polarised along the direction $\epsilon_{2p'}$, and hence

$$dQ\{(2p) \to (2p')\} = 0 \tag{26}$$

When $\mathbf{H}_0$ lies along the x-axis, therefore, $[\mathbf{r} \times \mathbf{M}_1]$ lies along the x-axis, and hence the scattered wave is polarised in the direction $\epsilon_{1p'}$. The average rate of energy transfer corresponding to the potentials (25) of a wave polarized in the direction ϵ perpendicular to r is

$$\frac{1}{8\pi} g_2^2 \frac{c\omega_0 (\omega_0^2 - \chi^2)^{3/2}}{r^4} (\epsilon, [\mathbf{r} \times \mathbf{M}_1])^2 \tag{27}$$

Denoting the angle between $\mathbf{r}$ and $\mathbf{M}_1$ by θ_1, using (24) and dividing by the rate of energy transfer (22) of the incident wave, we get the differential cross-section for the case $(2\,p) \to (1\,p')$

$$dQ'\{(2p) \to (1p')\} = \frac{g_2^4}{\mathbf{I}^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2 \omega_0^2} \sin^2\phi \sin^2\theta_1 \, d\Omega. \tag{28}$$

Denote by θ_0 the angle between $\mathbf{r}$ and $\mathbf{M}_0$. The relations between the various directions are shown in Fig. 1. We shall have to make repeated use of the well-known theorem that if ABC be a spherical triangle, then

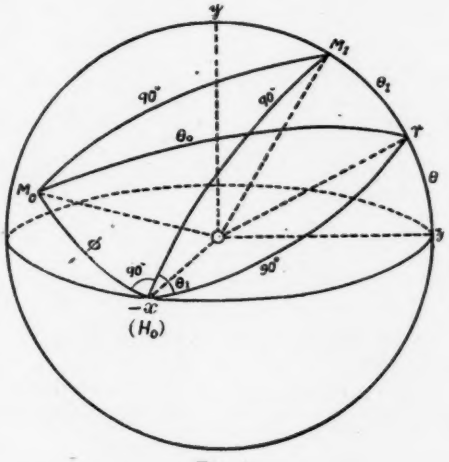

FIG. 1

$$\text{Cos AB} = \text{Cos AC. Cos BC} + \text{Sin A C. Sin BC} \cdot \text{Cos } \hat{\text{ACB}}. \tag{29}$$

Now since $r\,\mathbf{H}_0$ and $\mathbf{M}_1\,\mathbf{H}_0$ are right angles, the angle $\mathbf{M}_1\,\hat{\mathbf{H}}_0\,r$ is equal to the angle $\mathbf{M}_1 r$, *i.e.*, θ_1. Since $\mathbf{M}_1\,\mathbf{M}_0$ is also a right angle, $\mathbf{M}_1$ is the pole of

the great circle $M_0 H_0$ and hence the angle $M_0 \hat{H}_0 M_1$ is a right angle. Thus the angle $M_0 \hat{H}_0 r$ is $\frac{\pi}{2} + \theta_1$. Now applying the equation (29) to the triangle $M_0 H_0 r$ it follows at once that

$$\cos \theta_0 = \cos M_0 r = \sin M_0 H_0 \sin H_0 r \cos M_0 \hat{H}_0 r = -\sin \phi \sin \theta_1.$$

Thus (28) simplifies to

$$dQ' \{(2p) \to (1p')\} = \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2 \omega_0^2} \cos^2 \theta_0 \, d\Omega \qquad (30\,a)$$

Averaging over all initial directions of the dipole replaces $\cos^2 \theta_0$ by 1/3, so that

$$dQ \{(2p) \to (1p')\} = \frac{1}{3} \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2 \omega_0^2} d\Omega \qquad (30\,b)$$

Next consider an incident wave polarised along ϵ_{1p}, so that $\mathbf{H}_0$ now lies along the y-axis. $\mathbf{M}_1$ must now lie in the x-z plane. Denote the angles made by $\mathbf{M}_0$ and $\mathbf{M}_1$ with the x-axis by ψ_0 and ψ_1 respectively, and the angle between $\mathbf{M}_0$ and the z-axis by η_0. The angles are represented in Fig. 2. Now

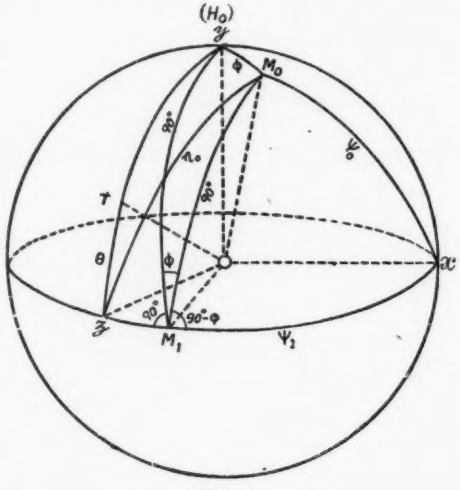

FIG. 2

since $y M_1$ and $M_0 M_1$ are right angles, angle $y \hat{M}_1 M_0$ = the angle $y M_0 = \phi$, and hence the angle $M_0 \hat{M}_1 x$ is $\frac{\pi}{2} - \phi$. Applying the identity (29) to the triangle $M_0 M_1 x$ it follows that

$$\cos \psi_0 = \cos M_0 x = \sin M_0 M_1 \cdot \sin M_1 x. \cos M_0 \hat{M}_1 x = \sin \psi_1 \cdot \sin \phi \qquad (31)$$

Applying the same identity to the triangle $\mathbf{M}_0\, z\, \mathbf{M}_1$ it follows that

$$\cos \eta_0 = \cos \mathbf{M}_0 z = \sin z\, \mathbf{M}_1 \cdot \sin \mathbf{M}_1\, \mathbf{M}_0 \cdot \cos z\, \hat{\mathbf{M}}_1\, \mathbf{M}_0 = -\cos \psi_1 \cdot \sin \phi. \quad (32)$$

Now consider the transition $(1\,p) \rightarrow (2\,p')$. The component of the vector potential (25) in the direction $\epsilon_{2p'}$ is

$$(\epsilon_{2p'} \cdot [\mathbf{r} \times \mathbf{M}_1]) = (\mathbf{M}_1 \cdot [\epsilon_{2p'} \times \mathbf{r}]) = |r| \cdot \mathbf{M}_{1x}$$

$\mathbf{M}_{1x}$ being the x component of $\mathbf{M}_1$, since $\epsilon_{2p'}$, and $\mathbf{r}$ both lie in the y-z plane. This is just $r\,|\mathbf{M}_1|\cos\psi_1$, and hence, using (22) and (27) and remembering (24), the differential cross-section for the case $(1\,p) \rightarrow (2\,p')$ can be deduced as before to be

$$dQ'\{(1p) \rightarrow (2p')\} = \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2\, \omega_0^2} \sin^2 \phi \cos^2 \psi_1\, d\Omega$$

$$= \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2\, \omega_0^2} \cos^2 \eta_0\, d\Omega \quad (33\,a)$$

in view of (32). Averaging over the initial orientations of the dipole, *i.e.*, over $\cos^2 \eta_0$, we get

$$dQ\{(1p) \rightarrow (2p')\} = \frac{1}{3} \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2\, \omega_0^2}\, d\Omega \quad (33\,b)$$

Finally consider the case $(1p) \rightarrow (1p')$. The component of $[\mathbf{r} \times \mathbf{M}_1]$ in the direction $\epsilon_{1p'} = \epsilon_{1p}$ is

$$(\epsilon_{1p} \cdot [\mathbf{r} \times \mathbf{M}_1]) = (\mathbf{r} \cdot [\mathbf{M}_1 \times \epsilon_{1p}]) = r\,|\mathbf{M}_1| \sin \psi_1 \sin \theta.$$

Hence, by a calculation similar to the one in the previous case we find

$$dQ'\{(1p) \rightarrow (1p')\} = \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2\, \omega_0^2} \sin^2 \theta \sin^2 \phi \sin^2 \psi_1\, d\Omega$$

which, by (31) reduces to

$$dQ'\{(1p) \rightarrow (1p')\} = \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2\, \omega_0^2} \sin^2 \theta \cos^2 \psi_0\, d\Omega \quad (34\,a)$$

Averaging over all initial directions of the dipole replaces $\cos^2 \psi_0$ by 1/3, so that finally

$$dQ\{(1p) \rightarrow (1p')\} = \frac{1}{3} \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2\, \omega_0^2} \sin^2 \theta\, d\Omega \quad (34\,b)$$

Summing over the final directions of polarisation of the scattered wave and averaging over the two transverse polarisations of the initial wave, *i.e.*, adding (26), (30 *b*), (33 *b*) and (34 *b*), and dividing by 2, we find

$$dQ = \frac{1}{6} \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2\, \omega_0^2} (2 + \sin^2 \theta)\, d\Omega \quad (35)$$

The integration of this over all angles gives the total cross-section

$$Q = \frac{16\pi}{9} \frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2 \omega_0^2}. \tag{36 a}$$

The exact classical formula given in A was

$$Q = 4\pi (\omega_0^2 - \chi^2)^2 \frac{\{a^2 \omega_0^2 + (\omega_0^2 - \chi^2)^3 + \chi^6\}}{\{a^2 \omega_0^2 + (\omega_0^2 - \chi^2)^3 + \chi^6\}^2 - 4a^2 \omega_0^2 \chi^6} \tag{36 b}$$

where $$a = 3\,Ic/2g_2^2,$$

which may be written correctly to within 2% in the simpler form

$$Q \simeq 4\pi \frac{(\omega_0^2 - \chi^2)^2}{a^2 \omega_0^2 + (\omega_0^2 - \chi^2)^3} \tag{36 c}$$

The formula (36 *a*) results from (36 *c*) if we neglect the effects of radiation reaction, *i.e.*, the second term in the denominator of (36 *c*).

Writing $E = c\hbar\omega_0$, $p = \hbar(\omega_0^2 - \chi^2)^{\frac{1}{2}}$, $g_2 = g_2' \hbar/\mu c$ and specialising the problem by putting $I = \hbar/2$ in order to apply it to the spin of a heavy particle (proton or neutron) we find that the expression which occurs in (30), (33) and (34) as a common factor is just

$$\frac{g_2^4}{I^2} \frac{(\omega_0^2 - \chi^2)^2}{c^2 \omega_0^2} = 4 \frac{g_2'^4}{\mu^4 c^4} \frac{p^4}{E^2}. \tag{37}$$

With this specialisation (36 *c*) may be written in the form

$$Q = 4\pi \frac{p^4}{\left(\frac{3}{4} \frac{\mu c^2}{g_2'^2}\right)^2 \mu^2 E^2 + p^6 \hbar^{-2}} \tag{36 d}$$

Discussion

We notice first that the quantum and classical theories agree in giving no scattering of longitudinally polarised mesons by the spin of the heavy particle in the approximation in which the heavy particle is taken as fixed.

The results of the previous two sections on the scattering of transversely polarised mesons are collected in the following table for the four cases considered.

	Usual Theory (quantum) charged mesons	New Theory (quantum) charged mesons	Quantum Theory neutral mesons	Classical Theory
	$(g'^4_2 p^4/\mu^4 c^4 E^2)\, d\Omega$	$(4g'^4_2 p^4/\mu^4 c^4 E^2)\, d\Omega$	$(4g'^4_2 p^4/\mu^4 c^4 E^2)\, d\Omega$	$(4g'^4_2 p^4/3\mu^4 c^4 E^2)\, d\Omega$
$dQ\{(2p) \to (2p')\}$	1	$\frac{1}{4}(\Delta Mc^2/E)^2 + \cdots$	0	0
$dQ\{(2p) \to (1p')\}$	1	$1-(\Delta Mc^2/E)+\cdots$	1	1
$dQ\{(1p) \to (2p')\}$	1	$1-(\Delta Mc^2/E)+\cdots$	1	1
$dQ\{(1p) \to (1p')\}$	1	$\sin^2\theta\left\{1-\left(\frac{\Delta Mc^2}{E}\right)+\cdots\right\}$	$\sin^2\theta$	$\sin^2\theta$

The first column gives the scattering of charged mesons on the usual quantum theory in which only the ordinary proton and neutron are assumed to exist. This is just given in each of the four cases by (20).

The next column gives the scattering on the basis of Bhabha's idea of allowing the heavy particles to exist in states of all integral charge. For a better comparison with the classical theory, we give the approximate expressions got by expanding in powers of $(\Delta Mc^2/E)$; namely (13 *b*), (14 *b*) and (16 *b*).

For scattering by a proton, a proton of charge $2e$ is virtually formed during the scattering process, so that ΔM has to be put equal to ΔM_2, the mass excess of a proton of charge $2e$ over an ordinary proton. For scattering by a neutron ΔM has to be put equal to ΔM_{-1} the mass excess of a negative proton over an ordinary proton. The two mass-excesses need not be the same. The scattering of positive and negative mesons is however exactly the same in every case.

The third column gives the quantum mechanical scattering of neutral mesons. This is derived from the second column by putting $\Delta M = 0$.

The last column gives the classical scattering as given by (26), (30 *b*), (33 *b*) and (34 *b*), and we have specialised the expressions by the substitution (37).

A comparison of the third and fourth columns shows that the quantum and classical theories give the same dependence on scattering angle and on the directions of polarisation of the incident and scattered meson for the scattering of neutral mesons. The expressions at the top of both columns are the same, except that the classical expression is smaller by a factor 3. This difference is not difficult to understand. It is a consequence of the averaging over the initial orientation of the spin of the heavy particle.

Consider the expression (30 *a*). An averaging over the initial direction of the spin of the heavy particle means that we have to average $\cos^2\theta_0$, where θ_0 is the angle between the initial direction of the spin of the heavy particle and the direction r. This averaging results in a factor 1/3. In this it must differ from the averaging over the initial orientation of the spin in the quantum theory, since, the spin being $\hbar/2$, the cosine of the angle it makes with any given direction can only be ± 1. Thus an averaging over the initial directions of the spin of the heavy particles gives a factor 1 in the quantum theory, instead of 1/3 as in the classical theory.* The same argument applies in the other two cases. This completely explains the only difference between the quantum mechanical and classical scattering of neutral mesons. The identity of the scattering in its dependence on energy, the scattering angle and the polarisation of the incident and scattered mesons shows that we may correctly use the classical formula to get the scattering of neutral mesons by a particle of spin $\hbar/2$ in the region of high energies where it differs from the quantum formula due to the effects of radiation reaction. The classical formula (36 *b*) would only go wrong seriously due to the appearance of quantum effects at energies comparable with or higher than the rest energy of the heavy particles, but for such high energies the scattering is already a small fraction of its value at the maximum due to the effects of radiation reaction.

A comparison of the second and third columns shows that the scattering of charged mesons on the assumption that the heavy particles can exist in states of all integral charge only differs from the scattering of neutral mesons by quantities of the order $\Delta Mc^2/E$. To a first approximation it is smaller by a factor $(1-\Delta Mc^2/E)$. Thus, on the basis of this assumption we see that the quantum mechanical scattering of charged mesons by the spin of the heavy particles shows complete correspondence with the classical scattering in its dependence on scattering angle and polarisation of the incident and scattered mesons. The dependence on energy is also very nearly the same, differing only by the correcting factor $(1-\Delta Mc^2/E)$ which varies little with energy. Due to this factor there will be a slight difference in the scattering by neutrons and protons since ΔM has to be put equal to ΔM_{-1} and ΔM_2 respectively in the two cases.

This complete correspondence is a further argument in favour of the assumption that the heavy particles can exist in states of all integral charge.

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* Had the heavy particle spin been $\hbar$, $\cos\theta_0$ could have taken on the values 1, 0 and -1, and hence the quantum mechanical average over the initial directions of the spin would have given 2/3 in this case instead of 1. For higher spins the quantum mechanical average is still smaller, and for larger and larger spin gradually approaches the classical average.

It also shows that the classical formula for the scattering of mesons multiplied by a factor 3 will give the scattering of *charged* mesons correctly to within 20% up to energies comparable with the rest energy of the heavy particles, as has already been suggested by one of us in a recent note.* Perhaps a more accurate formula could be obtained by multiplying the classical formula (36 *d*) by the factor $3\,(1-\Delta Mc^2/E)$ for the reasons mentioned above, thus

$$Q\,(\text{charged}) = 12\pi \frac{p^4}{\left(\frac{3}{4}\frac{\mu c^2}{g'^2_2}\right)^2 \mu^2 E^2 + p^6 \hbar^{-2}} \left(1-\frac{\Delta Mc^2}{E}\right). \qquad (36\,e)$$

A comparison of the first and last columns shows that there is no correspondence between the scattering on the usual quantum theory and the classical theory either in its dependence on scattering angle or in its dependence on the polarisation of the incident and scattered meson.

The scattering of charged mesons due to the spin of the heavy particles as calculated by Heitler and Ma (1940 formula 23 *c*) with Heitler's further assumption of allowing the heavy particles to exist in states of higher spin shows no correspondence with any classical theory. As the authors themselves have pointed out, the scattering vanishes if the mass excesses of the states of higher spin and charge are put equal to zero. In contrast to this, the results of the present paper show that the correspondence with the classical scattering by the spin becomes even greater when the mass excesses of the higher charge states are put equal to zero.

Summary

It is shown that the scattering of neutral mesons *by the spin of the heavy particles* (g_2 interaction) on the quantum theory agrees completely in its dependence on energy, scattering angle, and polarisation of the incident and scattered meson with the scattering on the classical theory (neglecting radiation reaction), except for being larger by a constant factor 3, which is due to differences in the averaging over the initial directions of spin of the heavy particle.

On the basis of the assumption put forward by Bhabha that the heavy particles can exist in states of all integral charge, it is shown that the scattering of charged mesons by the spin of the heavy particles only differs from the scattering of neutral mesons by factors $(1-\Delta M_2 c^2/E)$ and $(1-\Delta M_{-1}c^2/E)$ for scattering by protons and neutrons respectively, ΔM_2 and ΔM_{-1} being

* Bhabha: *Physical Review*, letter to the Editor.

the mass excesses of protons of charge $2e$ and $-e$ over an ordinary proton, and E being the meson energy. *Thus on this assumption the scattering of charged mesons shows complete correspondence with the classical theory*, and hence the previously given classical formula (36 *d*) taking radiation reaction into account multiplied by a factor 3 will give the scattering of charged mesons up to energies of roughly 10^9 e.v., correctly to within about 20%.

A new formula (36 *e*) is given tentatively which should be more accurate.

The scattering of charged mesons on the usual quantum theory shows no correspondence with the classical scattering. The scattering on the basis of Heitler's idea of allowing the heavy particles to exist in higher spin states also shows no correspondence with the classical scattering.

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RAMAN SPECTRUM OF GYPSUM

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Received December 5, 1940

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction*

The selection rules for the Raman effect in crystals belonging to the seven classes of symmetry have been given by Placzek (1930). Detailed experimental studies with single crystals of sodium nitrate (Nedungadi, 1939), calcite (Bhagavantam, 1940) and quartz (Saksena, 1940) and the discussion of these results by the author (Saksena, 1940) have shown that the selection rules are, in general, obeyed by these crystals, all of which possess trigonal symmetry. An extension of these studies to crystals having other symmetries is obviously of great interest. In the present communication the author has made a preliminary investigation with gypsum which is a crystal belonging to the monoclinic class of symmetry.

2. *Crystal Structure of Gypsum and Selection Rules*

Gypsum is an ionic crystal and the unit cell contains four molecules of $CaSO_4 \cdot 2\,H_2O$. It has only one symmetry axis, called the *b*-axis, which is perpendicular to the cleavage plane. The space group is $C_2{}^3{}_h$ and the character table as given by Bhagavantam (1938) is given in Table I.

Table I

Character Table for Gypsum Crystal

C_2^h	E	C_2	i	σ	r_i	External		$n_i{}^1$	Raman	Infra-red
						T	R			
A_1 ..	1	1	1	1	16	0	6	10	*p*	*f*
A_2 ..	1	−1	1	−1	20	0	12	8	*p*	*f*
B_1 ..	1	1	−1	−1	16	1	5	10	*f*	*p*
B_2	1	−1	−1	1	20	2	10	8	*f*	*p*
U_r ..	24	8	0	0						
$h_j\chi_j 1$ ..	72	−8	0	0						

It will be seen that there are altogether thirty-six Raman-active vibrations of which eighteen are classed as internal and the rest as external vibrations. These vibrations fall under two groups. Those which come under Class A_1 are symmetric and those coming under A_2 are antisymmetric to the *b*-axis. Their behaviour in transverse light scattering in directional excitation is stated in Table II.

Table II shows that when the symmetry axis is along the direction of observation OY, the anti-symmetric vibrations disappear when the electric vector is along OZ, and the symmetric vibrations disappear when the electric vector is along OY. On analysis with a double-image prism and with the axis of symmetry in the direction of illumination OX, the symmetric vibrations should appear only in the OZ component, and the anti-symmetric vibrations should appear only in the OX component. In the above table, OX and OY are the directions of illumination and observation respectively, and OZ is perpendicular to both these directions. These directions are always orientated along the directions of the three indicatrices of the crystal.

3. Experimental Arrangements

The instrument used for recording the spectra was a Zeiss three-prism glass spectrograph, and the spectra were obtained with two different single crystals of gypsum. The spectra (*a*), (*b*) and (*c*) reproduced in Fig. 1 and the spectrum (*j*) reproduced in Fig. 4 were obtained with a large piece of gypsum in which the direction of only one of the indicatrices—namely, the '*b*' axis was known. The spectra (*c*), (*b*) and (*a*) were taken with the symmetry axis along the directions of observation, illumination, and the direction perpendicular to both these respectively. The spectrogram (*j*) was taken with a camera of higher dispersion. The rest of the spectra were taken with a suitably cut crystal of smaller size in which the directions of the three indicatrices were known, and were perpendicular to the three plane faces of the crystal which was cut in the form of a rectangular parallelopiped. The spectra (*d*) and (*e*) were obtained with natural light and light polarised along OZ respectively, the crystal being so orientated that the symmetry axis was along the direction of observation OY. The polarisation pictures (*f*), (*g*), (*h*) and (*i*) were obtained with natural light the symmetry axis being along the direction of illumination for (*f*) and (*g*) and perpendicular to the directions of observation and illumination for the spectra (*h*) and (*i*). On account of the small size of the crystal, these spectra are insufficiently exposed. The orientation of the crystal, the directions of the electric vectors in the incident light (I.L.) and the scattered light (S.L.) are marked by appropriate symbols on the spectrograms.

TABLE II

(Illumination along OX; Observation along OY)

Nature of vibration	Tensor component	Symmetry axis along	Depolarisation			Total Intensities		
			Electric vector along OY	Electric vector along OZ	Electric vector along OY and OZ	Electric vector along OY	Electric vector along OZ	Electric vector along OY and OZ
Symmetric ..	$\epsilon_{\alpha\alpha} = a, \epsilon_{\beta\beta} = b$	OZ	∞	0	$\frac{d^2}{c^2}$	d^2	c^2	$d^2 + c^2$
	$\epsilon_{\gamma\gamma} = c, \epsilon_{\alpha\beta} = d$	OY	f	$\frac{d^2}{a^2}$	$\frac{d^2}{a^2}$	0	$d^2 + a^2$	$d^2 + a^2$
	$\epsilon_{\alpha\gamma} = 0, \epsilon_{\beta\gamma} = 0$	OX	0	0	0	d^2	b^2	$d^2 + b^2$
Anti-symmetric ..	$\epsilon_{\alpha\alpha} = \epsilon_{\beta\beta} = \epsilon_{\gamma\gamma} = 0$	OZ	0	∞	$\frac{a^2}{b^2}$	b^2	a^2	$b^2 + a^2$
	$\epsilon_{\alpha\beta} = 0, \epsilon_{\alpha\gamma} = a$	OY	$\frac{b^2}{a^2}$	f	$\frac{b^2}{a^2}$	$b^2 + a^2$	0	$b^2 + a^2$
	$\epsilon_{\beta\gamma} = b$	OX	∞	∞	∞	a^2	b^2	$b^2 + a^2$

[γ axis is taken as the symmetry axis in the above table.]

The positions of the two indicatrices perpendicular to the symmetry axis were fixed by putting the crystal plate between two crossed polaroid discs, on which the directions of the electric vectors were marked, and adjusting the plate for extinction.

4. Results and their Discussion

The Raman spectrum of gypsum has been investigated by several previous workers. In Table III, the frequency shifts of Raman lines reported by these authors are listed along with those observed in the various spectrograms obtained in the present investigation. The numbers given within brackets against ν_1, ν_2, ν_3 and ν_4 are the Raman frequencies of the free SO_4 ion.

TABLE III

Raman Frequencies of Gypsum

Class of vibration	Krishnan (1929)	Krishnamurti (1930)	Nisi (1931)	Cabannes (1932, 1938)	Rassetti (1932)	Author
Lattice ..					37, 60	80
					110, 122	125
					134, 146	
			183		164, 182	175
			311		211	315
ν_2 (454) ..			415	414	415	415
		484	493	495	495	492
ν_3 (622) ..						585
			617	620		618
		667	672	671	672	672
ν_1 (983) ..	1011	1006	1006	1009	1009	1006
ν_4 (1106) ..			1114			1065?
						1115
	1134	1132	1135	1136	1137	1136
Water band ..	3240					
	3397		3404	3404	3399 / 3426	3406
	3493		3497	3495		3493

It will be noticed that there is general agreement between the results of different authors regarding the frequencies of lines at 415, 495, 618, 672, 1006 and 1136. The presence of a line at 1115 reported by Nisi has been

confirmed by the author. In addition, two new lines at 585 and 1065 have been observed. As shown in Table I, the degeneracies arising from the tetrahedral symmetry of the SO_4 group are no longer present in the crystal on account of a lower order of symmetry for the latter. Thus the four frequencies characteristic of the SO_4 ion in solutions of sulphates should be split up into at least nine distinct frequencies in the crystal as indicated by Bhagavantam. This conclusion from the group-theoretical analysis is substantiated by the results of the present investigation. Thus together with the weak lines 585 and 1065 observed here, nine frequencies are present in the region 400–1200 and these are grouped together in Table II against the corresponding frequencies of the SO_4 ion. Further multiplication of the lines due to the presence of four SO_4 groups in the unit cell of the crystal as suggested by the character table is not however observed. This may probably be due to the fact that the shift of the lines due to this cause is too small to be observed by an ordinary spectrograph.

In addition to the above-mentioned frequencies characteristic of the SO_4 group Rassetti (1932) has reported nine low frequency lines at 37, 60, 110, 122, 134, 146, 164, 182 and 211 cm.$^{-1}$ In their place Nisi (1931) has recorded only two lines at 183 and 311. In the present investigation, the author has observed four lines at 80, 125, 175 and 315. Theoretically, however, eighteen Raman frequencies which may be classified as lattice oscillations could be expected. A more detailed investigation of this region appears to be desirable.

The presence of two water-bands at 3406 and 3493 is well established. The author has been unable to confirm neither the presence of a third band at 3240 reported by Krishnan (1929) nor the splitting observed by Rassetti (1932) for the band 3406. The interesting features of the polarisation of all the Raman lines will be discussed in the next section.

5. *Intensity and Polarisation of Raman Lines*

Tables IV and V give visual estimates of intensity of Raman lines for specified directions of incidence and observation with respect to the symmetry axis of the crystal and with incident light (*a*) polarised, (*b*) unpolarised. The directions OX, OY and OZ are along the directions of the three indicatrices perpendicular to the three end faces of the crystal.

TABLE IV

Incident Light Unpolarised

(Illumination along OX ; Observation along OY)

Frequencies	*b*-axis along OX		*b*-axis along OZ	
	Component of scattered light		Component of the scattered light	
	Along OX	Along OZ	Along OX	Along OZ
Spectrogram number	3 (*g*)	3 (*f*)	3 (*i*)	3 (*h*)
415	0	1		
493	0	1		
618	1	0		
672	2	0		
1006	0	7	4	2
1136	4	0	1	0

TABLE V

Frequencies	Only one of the directions OX, OY and OZ fixed with respect to the crystal, incident light unpolarised and the symmetry axis along			The directions OX, OY and OZ along the three indicatrices. The symmetry axis along OY and incident light	
	OZ	OX	OY	Unpolarised	Polarised along OZ
Spectrogram number	1 (*a*)	1 (*b*)	1 (*c*)	2 (*d*)	2 (*e*)
80	2	2	..	..	..
125	..	3	..	..	..
175	5	1			
315	1	1			
415	5	1	..	2	1
492	2	5	3	6	3
585		1			
618	3	3	1	3	0
672	2	3	1	1	0
1006	10	10	8	10	6
1065		1	1		
1115	1	1		1	
1136	5	7	3	5	0
3406	0	2		4	1
3495	5	2		1	

Cabannes (1938) has studied the polarisation characters of some of the Raman lines of gypsum by using a single crystal with three nearly normal faces one of which is parallel to the cleavage plane. His main conclusions

are that the frequencies 1006, 415 and 492 are symmetric and 672 is anti-symmetric, and that the lines 620 and 1136 behave as though they are due to a superposition of both symmetric and anti-symmetric vibrations. Further, according to him both the water-bands belong to the symmetric class. Nisi (1931) has also investigated the variations in intensities of lines for different orientations of the crystal. He failed to observe any change in the intensity for any of the lines except those at 415 and 493. According to him when one of these two lines has a maximum intensity, the other has a minimum intensity. He also found that the two water bands behaved differently for different crystal orientations.

In the present investigation it was observed (see spectrogram 2 *e*) that when the incident light is polarised along OZ and the symmetry axis is along OY, the lines 1136, 672 and 618 are either absent or very weak while those at 415, 492, 1006 and 3406 are clearly recorded. Reference to Table II will show that the former group of lines belongs to the anti-symmetric vibrations and the latter group to the symmetric class. This conclusion is further substantiated by the polarisation pictures, Fig. 3 (*f*) and Fig. 3 (*g*) taken with polarised light when the symmetry axis is along the direction of illumination OX. The frequencies 1006, 492 and possibly 415, appear only in the OZ component (3 *f*), while the lines 1136, 672 and 618 appear only in the OX component (3 *g*). As stated in Table II, the former therefore represent totally symmetric vibrations and the latter anti-symmetric ones. These conclusions are in substantial agreement with the results of Cabannes quoted above. Since according to group-theoretical analysis eighteen lines should be present in the crystal whereas only nine have been observed, it is probable that some of these lines are combinations of symmetric and anti-symmetric vibrations. This question could be decided only by giving long exposures and obtaining more intense pictures in order to bring out the feeble component of these lines in the complementary spectrum of 3 (*f*) and (*g*).

Further, according to Table II, the symmetric vibrations will have a polarisation d^2/c^2 when the incident light is unpolarised and the symmetric axis is along OZ. The observed depolarisation of the totally symmetric vibration 1006 as shown in Figs. 3 (*h*) and (*i*) is, therefore, in agreement with this theoretical expectation. Spectra 1 (*a*) and (*b*) show large variations in the intensities of lines 415, 492 125 and 175; 415 and 175 are strong and 492 and 125 are weak in Fig. 1 (*a*) while the former are weak and the latter strong in Fig.1 (*b*).

In accordance with the observations of Nisi, the water-bands also reveal similar variations of intensity with crystal orientation. The tensor

components given in Table II lead us to the conclusion that the symmetric vibrations should show large variations of intensity for different directions of the crystal. Presumably the alternation of intensity of the two water-bands indicates, as suggested by Cabannes, that they are both totally symmetric. This statement, however, requires reconsideration as only one of the directions OX, OY and OZ is fixed relative to the crystal in the present investigation.

6. *Summary*

The spectra of a single crystal of gypsum are obtained in various orientations, and the state of polarisation of some of the lines is also studied. Four new lines at 80, 125, 585 and (1065) have been obtained by the author besides the lines 175 and 315 reported only by Nisi. Spectra of gypsum have also been obtained with incident light polarised along OZ, the symmetry axis being along OY, the direction of observation. The polarisation studies and the results obtained with polarised incident light completely satisfy the selection rules for a monoclinic crystal. This enables us to classify the lines 415, 492 and 1006, as totally symmetric vibrations, and 618, 672 and 1136 as antisymmetric ones.

In conclusion, the author expresses his gratitude to Sir C. V. Raman for his kind interest in the work and for affording the facilities for carrying out the investigation.

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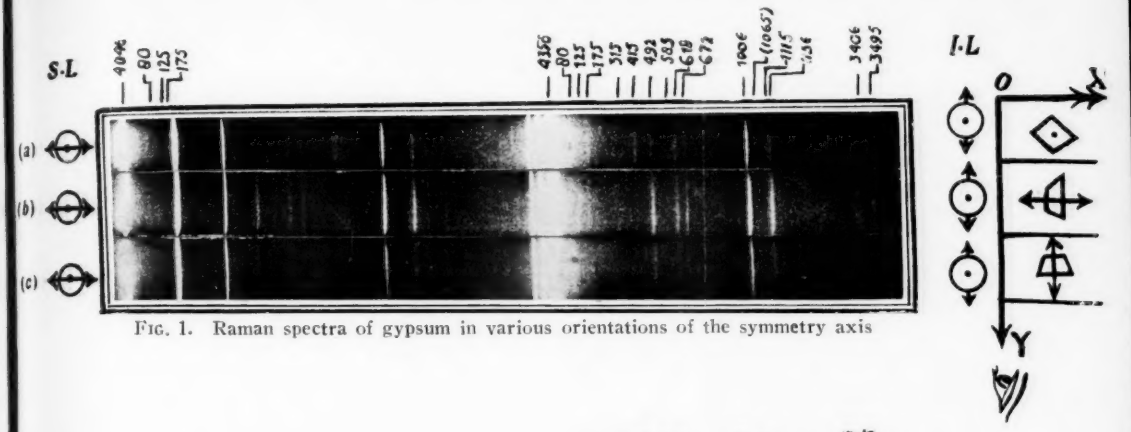

FIG. 1. Raman spectra of gypsum in various orientations of the symmetry axis

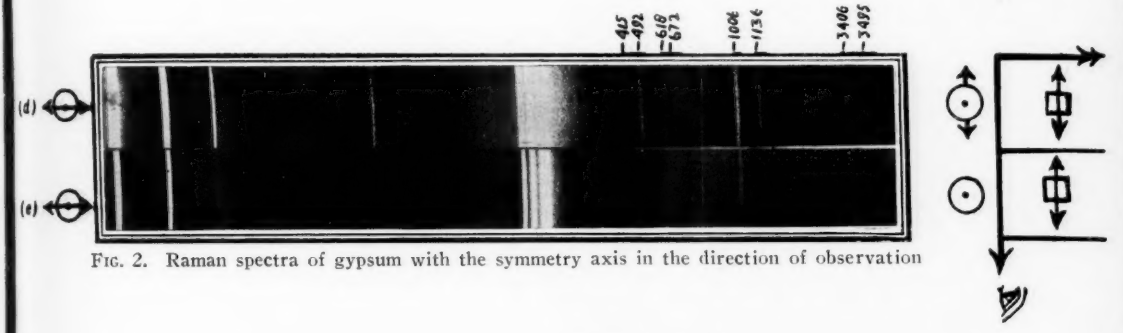

FIG. 2. Raman spectra of gypsum with the symmetry axis in the direction of observation

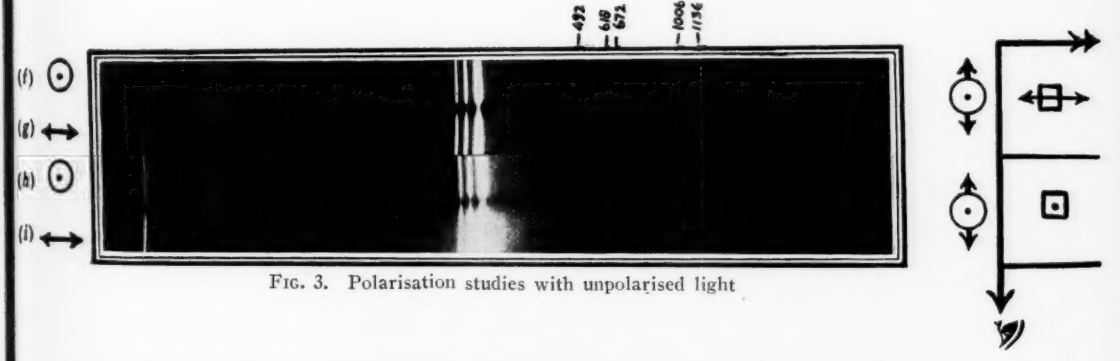

FIG. 3. Polarisation studies with unpolarised light

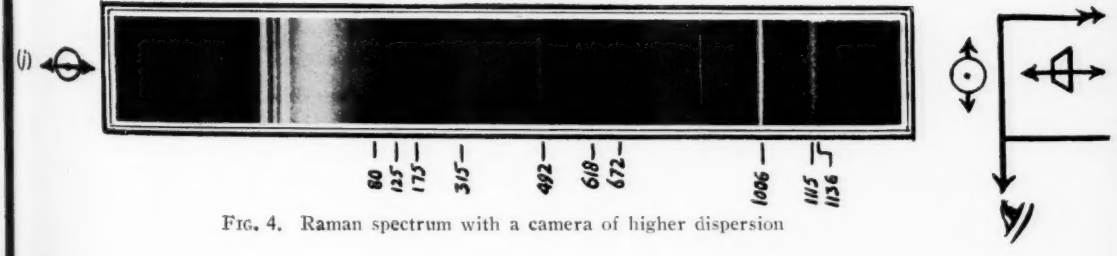

FIG. 4. Raman spectrum with a camera of higher dispersion

STUDIES IN NAPHTHALENE SERIES

Part VI. Synthesis of 2-Propyl-1-Naphthol and Properties of 2-Propionyl-1-Naphthol

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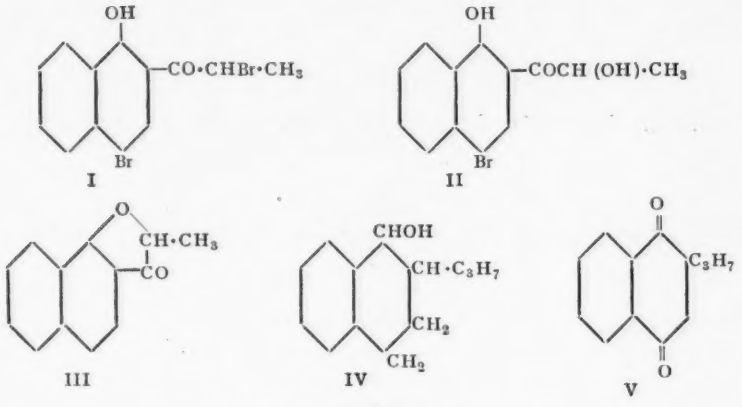
Received October 21, 1940

As a continuation of the scheme outlined in Part I of this series,[1] we have prepared 2-Propyl-1-naphthol by the Clemmenson Reduction of 2-propionyl-1-naphthol which was prepared by a slight modification of Hantzsch's method.[2] As stated in Part I, it was impossible to avoid the formation of acidic as well as neutral by-products in small quantities. 2-Propionyl-1-naphthol gave readily the picrate, the semicarbozone, phenylhydrazone, the *p*-nitrophenylhydrazone, and the methyl ether (Robertson's method). It is not affected by heating with glacial acetic or propionic acids in the presence of anhydrous zinc chloride. Bromination gives mono- as well as dibromo-derivatives. The constitution of the mono-bromo-derivative which has also been prepared by Hantzsch is shown to be 4-bromo-2-propionyl-1-naphthol, as the chromone obtained by Kostanecki's method, gave 4-bromo-1-hydroxy-2-naphthoic acid on alkaline hydrolysis. The dibromo-derivative had the constitution represented by (1) as under the action of alkali solution it gave 2-lactyl-1-naphthol (II) as well as 5-bromo-2-methyl-α-naphtha-coumaranone (III). Nitration with one mol of fuming nitric acid gave 4-nitro-2-propionyl-1-naphthol, as its chromone gave 4-nitro-1-hydroxy-2-naphthoic acid on alkaline hydrolysis. However, two mols or excess of nitric acid gave exclusively 2 : 4-nitro-1-naphthol owing to the extrusion of the propionyl group.

A considerable amount of a neutral, hydroxylic compound was formed during the Clemmenson Reduction of 2-propionyl-1-naphthol to 2-propyl-1-naphthol. This has been provisionally assumed to be 2-propyl-ac-tetrahydro-1-naphthol (IV) from the analysis and general properties. 2-Propyl-1-naphthol which has been characterised by its picrate and methyl ether coupled readily with benzendiazonium chloride giving benzene-azo-3-propyl-4-naphthol, and an isomeric, neutral compound having the hydrazone structure (V) as its acid hydrolysis gave 2-propyl-α-naphthaquinone. Further work with the specific aim of preparing the azo dyes from 2-propionyl-1-naphthol is being continued.



Experimental

2-*Propionyl*-1-*naphthol*-α-naphthol (75 g.) is slowly added to a warm solution of anhydrous zinc chloride (120 g.) in propionic acid (120 c.c.), and the solution heated to boiling on sand-bath for three hours. The warm solution is now poured into a large quantity of water (700 c.c.) containing some hydrochloric acid, when a coloured solid settles down. The supernatant liquid is decanted off, and the solid crystallised from alcohol when pale-yellow, square plates of 2-propionyl-1-naphthol crystallises out. The alcoholic mother-liquor is evaporated to dryness, and the coloured residue is purified through 10 per cent. caustic soda solution. The solid recovered on acidification gives further amount of the same ketone (yield = 65 per cent.). The recrystallised samples melt at 85°, and its alcoholic solution gives a dark-green colouration with ferric chloride.

The Picrate crystallised from hexane in long, red needles, m.p. 88° (depressed to 74° by the original ketone).

(Found: C, 53·0; H, 3·7. $C_{19}H_{15}O_9N_3$ requires C, 53·1; H, 3·5 per cent.)

The Semicarbozone crystallised from glacial acetic acid in yellow, small plates, m.p. 304°.

(Found: C, 65·3; H, 5·8. $C_{14}H_{13}O_2N_3$ requires C, 65·4; H, 5·8 per cent.)

The Phenylhydrazone crystallised from alcohol in lustrous, white plates, m.p. 78° (depressed to 61° by the original ketone).

(Found: C, 78·5; H, 6·1. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2 per cent.)

The p-*nitrophenylhydrazone* crystallised from alcohol in red plates, m.p. 232°.

(Found: N, 12·2. $C_{19}H_{17}N_3O_3$ requires N, 12·5 per cent.)

The methyl ether crystallised from hexane in white needles, m.p. 45°.

(Found : C, 78·2 ; H, 6·6. $C_{14}H_{14}O_2$ requires C, 78·5; H, 6·5 per cent.)

2-Propionyl-1-naphthol remained unaffected when heated with glacial acetic acid or propionic acid in presence of anhydrous zinc chloride. Leaving it in contact with anhydrous aluminium chloride in nitrobenzene solution gave a product unmelted below 300° and giving a dark-green coloration with ferric chloride.

(Found: C, 79·4; H, 5·3. $C_{28}H_{22}O_4$ requires C, 79·6; H, 5·2 per cent.)

Kostanecki Reaction with 4-*bromo*-2-*propionyl*-1-*naphthol and formation of* 6-*bromo*-2 : 3-*dimethyl*-1 : 4-α-*naphthapyrone.*—A mixture of 4-bromo-2-propionyl-1-naphthol (5 g.), anhydrous sodium acetate (15 g.) and acetic anhydride (25 c.c.) was heated in an oil-bath at 180–85° for ten hours with constant shaking. The solid obtained by pouring the mixture into water was triturated with 5 per cent. alkali in the cold to remove the unchanged material, and the residue crystallised from glacial acetic acid when the *pyrone* was obtained in white, long, silky needles, m.p. 225°.

(Found: Br, 26·4. Calc. for $C_{15}H_{11}O_2$ Br. Br, 26·4 per cent.)

The chromone dissolves in concentrated sulphuric acid without giving any colour or fluorescence. Chakravarti and Bagchi[3] who have prepared this chromone by the application of Simonis Reaction between 4-bromo-1-naphthol and C-methyl-aceto-acetic ester record the m.p. as 211–12°.

Hydrolysis of the above pyrone by alkali to 4-*bromo*-1-*hydroxy*-2-*naphthoic acid.*—The pyrone (1 g.) was heated with 10 per cent. NaOH (20 c.c.) on the sand-bath under reflux for three hours. The filtered solution, on acidification with concentrated hydrochloric acid gave an acid, which after purification through sodium bicarbonate solution crystallised from alcohol in needles, m.p. 245–46°. This was identified as 4-bromo-1-hydroxy-2-naphthoic acid by comparison with an authentic specimen.

4-*Bromo*-2-α-*bromopropionyl*-1-*naphthol.*—The solution of bromine (1 : 1 c.c.) in glacial acetic acid (10 c.c.) was gradually added to the solution of 2-propionyl-1-naphthol (2 g.) in the same solvent (25 c.c.). After the addition of a trace of iodine, the solution is heated on water-bath for three hours

when copious evolution of hydrogen bromide takes place. The cooled solution deposited a solid which crystallised from glacial acetic acid in sulphur-yellow needles, m.p. 145°.

(Found: Br, 44·7. $C_{13}H_{10}O_2Br_2$ requires Br, 44·7 per cent.)

The dibromoderivative is sparingly soluble in alcohol and cannot be further brominated.

Action of caustic soda solution on the dibromoderivative.—The solution of the dibromoderivative (1 g.) in 10 per cent. caustic alkali (15 c.c.) was heated on the water-bath under reflux for two hours. The cooled filtered solution gave a solid which crystallised from alcohol in yellow, micro-crystalline plates, m.p. 214°. There was practically no neutral product.

(Found: Br, 27·2. $C_{13}H_{11}O_3$ Br requires Br, 27·1 per cent.)

Action of sodium methoxide on the dibromoderivative, and formation of 4-*bromo*-2-*acrylyl*-1-*naphthol, and* 5-*bromo*-2-*methyl-naphtha-coumaranone.*—A solution of the dibromoketone (2 g.) in sodium methoxide (2 g. Na; 50 c.c. methyl alcohol) was heated under reflux on water-bath for two hours. The residue left after the removal of alcohol was treated with hot water and dilute NaOH, and the insoluble portion filtered off. The neutral portion crystallised from alcohol in small, yellow plates, m.p. 252°.

(Found: Br, 28·7. $C_{13}H_9O_2Br$ requires Br, 28·9 per cent.)

The alkaline, aqueous filtrate was acidified, when a yellow solid which crystallised from hexane as a micro-crystalline powder, m.p. 204· was obtained.

(Found: Br, 28·9. $C_{13}H_9O_2$ Br requires Br, 28·9 per cent.)

Nitration of 2-*propionyl*-1-*naphthol and formation of* 4-*nitro*-2-*propionyl*-1-*naphthol.*—A solution of fuming nitric acid, $d. = 1·5$ (0·7 c.c.) in glacial acetic acid (10 c.c.) is gradually added with constant shaking to a cooled solution of the ketone (3 g.) in glacial acetic acid (40 c.c.). A yellow solid begins to separate out at once, and the solid is filtered off after keeping the mixture for one hour. It crystallised from alcohol in long, yellow needles, m.p. 162°, and easily dissolved in alkali solution with a yellow colour (yield = 85 per cent.).

(Found: C, 63·4; H, 4·5. $C_{13}H_{11}NO_4$ requires C, 63·7; H, 4·5 per cent.)

Kostanecki Reaction with 4-*nitro*-2-*propionyl*-1-*naphthol and formation of* 6-*nitro*-2: 3-*dimethyl*-1 : 4-α-*naphthapyrone.*—A mixture of 4-nitro-2-propionyl-1-naphthol (5 g.), anhydrous sodium acetate (10 g.) and acetic anhydride (25 c.c.) was heated at 100° for two hours, then at 120° for three hours, and

finally at 140° for six hours. The solid obtained by pouring the mixture into water was triturated with dilute alkali and crystallised from glacial acetic acid when the *pyrone* was obtained in pale-yellow needles, m.p. 226°.

Its solution in concentrated sulphuric acid did not develop any colour or fluorescence.

(Found: C, 66·7; H, 4·2. $C_{15}H_{11}O_4N$ requires C, 66·9; H, 4·1 per cent.)

Hydrolysis of the above chromone to 4-nitro-1-hydroxy-2-naphthoic acid.—The chromone (1 g.) was hydrolysed as usual by heating on sand-bath under reflux with 10 per cent. NaOH (20 c.c.). The acid obtained on acidifying the alkaline solution was purified through sodium bicarbonate solution and crystallised from alcohol in pale-yellow needles, m.p. 221°, undepressed by admixture with an authentic specimen of 4-nitro-1-hydroxy-2-naphthoic acid. During the nitration of 1-hydroxy-2-naphthoic acid with fuming nitric acid in glacial acetic acid, if sufficient care is not taken in cooling and shaking the mixture, the yield of the nitrated acid falls down considerably, and a large amount of 2-nitro-1-naphthol is formed.

Nitration of 2-propionyl-1-naphthol with two or more mols of nitric acid.—The nitration was carried out as usual using 0·5 c.c. of fuming nitric for 1 gm. of the ketone. The solid obtained by pouring the mixture into water after 12 hours was identified at 2:4-dinitro-1-naphthol.

Clemmenson Reduction of 2-propionyl-1-naphthol and formation of 2-propyl-1-naphthol and 2-propyl-ac-tetrahydro-1-naphthol.—A mixture of 2-propionyl-1-naphthol (20 g.), amalgamated zinc (30 gm.) and dilute hydrochloric acid (100 c.c.) was heated under reflux on sand-bath for 12 hours. The oily substance that floated on the surface of the cooled mixture was extracted with ether, and the acidic product was extracted with alkali. The alkaline solution on acidification gave an oil which was recovered by extraction with ether. *2-Propyl-1-naphthol* was obtained as a thick, dark-brown oil, b.p. 165°/6 mm. (yield = 50 per cent.).

(Found: C, 83·8; H, 7·6. $C_{13}H_{14}O$ requires C, 83·9; H, 7·5 per cent.)

The Picrate crystallised from benzene in red needles, m.p. 113° (depressed to 97° by picric acid).

(Found: C, 54·6; H, 4·3. $C_{19}H_{17}O_8N_3$ requires C, 54·9; H, 4·1 per cent.)

The ethereal solution, from which 2-propyl-1-naphthol was extracted with alkali gave, on evaporation, an oil with a characteristic smell. It boiled

at 120–21°/7 mm. and did not form a picrate. Its ethereal solution reacted slowly with sodium liberating hydrogen.

(Found: C, 81·8; H, 9·7. $C_{13}H_{18}O$ requires C, 82·1; H, 9·5 per cent.)

The methyl ether of 2-propyl-1-naphthol, obtained by the alkali-dimethylsulphate method, was a thick-brown boil, b.p. 145°/6 mm.

(Found: C, 83·6; H, 8·1. $C_{14}H_{16}O$ requires C, 84·0; H, 8·0 per cent.)

Coupling of 2-propionyl-1-naphthol with benzene diazonium chloride and isolation of benzene-azo-3-propyl-4-naphthol and the phenyl hydrazone of 2-propyl-α-naphthaquinone.—An ice-cold diazolised solution of aniline (1 g.) in hydrochloric acid was gradually added to the alkaline solution of 2-propyl-1-naphthol (2 g.), and the red-dye that separated out was filtered off. The solid was treated with 5 per cent. NaOH solution and the alkali insoluble portion was filtered off. The alkaline solution, on acidification, gave a solid which crystallised from hexane in deep-red, small plates, m.p. 180°.

(Found: C, 78·5; H, 6·3. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2 per cent.)

The alkali-insoluble product crystallised from alcohol in small, dark-red plates, m.p. 112°.

(Found: C, 78·2; H, 6·2. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2 per cent.)

The neutral product was heated with dilute hydrochloric acid on sand-bath under reflux for four hours; and the solid that separated out on cooling was filtered off. It crystallised from alcohol in brown, small plates, m.p. 243°.

(Found: C, 77·6; H, 6·2. $C_{13}H_{12}O_2$ requires C, 78·0; H, 6·0 per cent.)

We take this opportunity of thanking Capt. M. Haider Khan, M.A., B.SC., Prof. R. N. Bhagwat, M.A., B.SC., and Rev. Father G. Palacios, S.J., PH.D., D.D., for their kind interest in this work, and provision of facilities.

Summary

2-Propyl-1-naphthol has been prepared by the Clemmenson Reduction of 2-propionyl-1-naphthol, the simple derivatives of which have been described. Bromination and nitration of 2-propionyl-1-naphthol under various conditions have been studied, and the constitution of the resulting products has been determined.

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STUDIES IN NAPHTHALENE SERIES

Part VII. Attempted Synthesis of 4-Stearyl-, 4-Palmityl-, and 4-Lauryl-1-naphthols

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Received October 21, 1940

In previous communications of this series, the synthesis of 4-acetyl, 2-stearyl-, 2-palmityl- and 2-lauryl-1-naphthols has been described,[1] and these have been found to be sufficiently interesting as intermediates for the preparation of azo-dyes and textile assistants. It appeared highly necessary to explore the methods of synthesising 4-stearyl-, 4-palmityl- and 4-lauryl-1-naphthols as these compounds are bound to be much more useful for the same purpose. Although our final objective has not been realised, we wish to place on record the interesting results so far obtained as it may be long before the interrupted work may be resumed.

The condensation of stearyl chloride with α-naphthol in the presence of anhydrous zinc chloride gave a very poor yield (5 per cent.) of 4-stearyl-1-naphthol, as the main product formed (80 per cent.) was its 2-stearyl-isomer, and the yield was not improved by using aluminium chloride, as it promoted the formation of 4 : 4′-dihydroxy-1 : 1′-dinaphthyl. This was surprising as 4-acetyl-1-naphthol was obtained in over 60 per cent. yield. When α-naphthol was replaced by its methyl ether, an excellent yield of the methyl ether of 4-stearyl-1-naphthol was obtained, but attempts to demethylate it in the presence of anhydrous aluminium chloride led to the simultaneous splitting off of the stearyl group as stearic acid. Its Clemmenson Reduction gave readily 1-methoxy-4-octadecyl-naphthalene, but its demethylation to 4-octadecyl-1-naphthol by anhydrous aluminium chloride did not lead to the encouraging results. As identical results are obtained by using palmityl and lauryl chlorides no further description of their products is necessary.

However, we have succeeded in preparing 4-stearyl-1-naphthol in good yield by condensing stearyl chloride with either 2-acetyl-1-naphthol, or 2-carbomethoxy-1-naphthol, and eliminating the acetyl and carboxyl groups from the resulting products, but the investigation is far from complete. This research as well as the condensation of long-chain unsaturated acids with α-naphthol will form the subjects of further communications.

Experimental

Condensation of stearyl chloride with α-naphthol and formation of 4-stearyl-1-naphthol.—α-Naphthol (20 g.) and stearyl chloride (30 g.) were alternately added to a suspension of finely powdered anhydrous zinc chloride (20 g.) in nitrobenzene (120 c.c.). After keeping the mixture at the room temperature for 48 hours, the zinc chloride was dissolved by adding ice-cold, dilute, hydrochloric acid, and the nitrobenzene steam-distilled off. The dry reddish-brown solid was exhaustively extracted with petroleum ether (b.p. 40–60°), when 2-stearyl-1-naphthol (80 per cent. yield) went in solution, and the insoluble residue crystallised from alcohol when fine, white needles of *4-stearyl-1-naphthol* (6 per cent. yield), m.p. 159–60° were obtained. It was soluble in alcohol, benzene, acetone, and acetic acid, but insoluble in hexane and petroleum ether. It was readily soluble in 5 per cent. caustic soda solution, thus differing fundamentally from its 2-isomer which is almost insoluble in the same medium. Its alcoholic solution gave violet coloration with ferric chloride.

(Found: C, 81·7; H, 10·1. $C_{28}H_{42}O_2$ requires C, 81·9; H, 10·2 per cent.)

Condensation of α-naphthyl methyl ether with stearyl chloride and preparation of 1-methoxy-4-stearyl-naphthalene.—Stearyl chloride (15 g.) dissolved in nitrobenzene (15 c.c.) was slowly added to a mixture of nitrobenzene (65 c.c.), powdered anhydrous zinc chloride (12 g.) and α-naphthyl methyl ether (8 c.c.). After keeping the mixture at the room temperature for 48 hours, it was worked up as usual. The dark-brown product that was obtained dissolved in alcohol on warming, leaving some residue (15 per cent.) which was identified as 4: 4′-dimethoxy-1: 1′-dinaphthyl.[2] The alcoholic solution, on cooling, deposited white, shining needles, m.p. 125–26° (yield = 70 per cent.).

1-Methoxy-4-stearyl-1-naphthalene was soluble in the usual organic solvents, and its alcoholic solution did not give any coloration with ferric chloride.

(Found: C, 81·8; H, 10·2. $C_{29}H_{44}O_2$ requires C, 82·1; H, 10·4 per cent.)

Attempts to demethylate 1-methoxy-4-stearyl-naphthalene to 4-stearyl-1-naphthol.—Finely powdered anhydrous aluminium chloride (3 g.) was gradually added to the solution of 4-stearyl-1-methoxy-naphthalene (2 g.) in dry benzene (60 c.c.) with thorough shaking, and warmed on water-bath for one hour and a half. After destroying aluminium chloride, the benzene was removed on the water-bath and the residue extracted with 5 per cent.

NaOH. The alkaline solution gave only stearic acid and α-naphthol on acidification with concentrated hydrochloric acid, and not a trace of 4-stearyl-1-naphthol.

Clemmenson Reduction of 1-*methoxy*-4-*stearyl-naphthalene to* 1-*methoxy* 4-*octadecyl-naphthalene*.—A solution of 1-methoxy-4-stearyl-naphthalene (2 g.) in alcohol (25 c.c.) was added to a flask containing amalgamated zinc (5 g.) and dilute hydrochloric acid (50 c.c.). After heating the mixture on sand-bath under reflux for 8 hours, the contents were decanted off into water, and extracted with ether. The residue left after the removal of ether crystallised from alcohol in small, white, lustrous needles, m.p. 202–03°.

(Found: C, 84·6; H, 11·3. $C_{29}H_{46}O$ requires C, 84·9; H, 11·2 per cent.)

1-*Methoxy*-4-*palmityl-naphthalene* was obtained in 65 per cent. yield using palmityl chloride. It was soluble in the usual organic solvents, and its alcoholic solution did not give any coloration with ferric chloride. Attempts to demethylate it by anhydrous aluminium chloride in dry benzene solution gave palmitic acid and α-naphthol.

(Found: C, 81·6; H, 10·2. $C_{27}H_{40}O_2$ requires C, 81·8; H, 10·1 per cent.)

1-*Methoxy*-4-*hexadecyl-naphthalene* obtained by the Clemmenson Reduction of the above product crystallised from alcohol in white needles, m.p. 224–25°. Soluble in the usual organic solvents, its alcoholic solution did not give any coloration with ferric chloride.

(Found: C, 84·6; H, 11·1. $C_{27}H_{42}O$ requires C, 84·8; H, 11·0 per cent.)

1-*Methoxy*-4-*lauryl-naphthalene* obtained in 70 per cent. yield using lauryl chloride crystallised from alcohol in small, lustrous flakes m.p. 111–12°. Soluble in the usual organic solvents, its alcoholic solution did not develop any colour with ferric chloride. It could not be demethylated to 4-lauryl-1-naphthol.

(Found: C, 81·0; H, 9·3. $C_{23}H_{32}O_2$ requires C, 81·2; H, 9·4 per cent.)

4-*Dodecyl*-1-*methoxy-naphthalene* obtained by the Clemmenson Reduction of the above product crystallised from alcohol in white, lustrous flakes m.p. 165–66°, and was soluble in usual organic solvents.

(Found: C, 84·3; H, 10·3. $C_{23}H_{34}O$ requires C, 84·5; H, 10·4 per cent.)

We are thankful to Prof. R. N. Bhagwat, M.A., B.Sc., and Rev. Father G. Palacios, S.J., D.D., Ph.D., for their kind interest in this work and provision of facilities.

Summary

4-Stearyl-1-naphthol is obtained in a poor yield by the Friedel-Crafts Reaction between stearyl chloride and α-naphthol as the main product is 2-stearyl-1-Naphthol. α-naphthylmethyl ether, however, gave an excellent yield of 1-methoxy-4-stearyl-naphthalene, but its demethylation by anhydrous aluminium chloride led to the simultaneous removal of the stearyl group. Clemmenson Reduction gave readily 1-methoxy-4-octadecyl-naphthalene. Similar results were obtained by using palmityl and lauryl chlorides.

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SYNTHETIC EXPERIMENTS IN THE BENZO-PYRONE SERIES

Part III. Syntheses of Coumarino- and Flavono-α-methyl-7 : 8-Dihydrofurans

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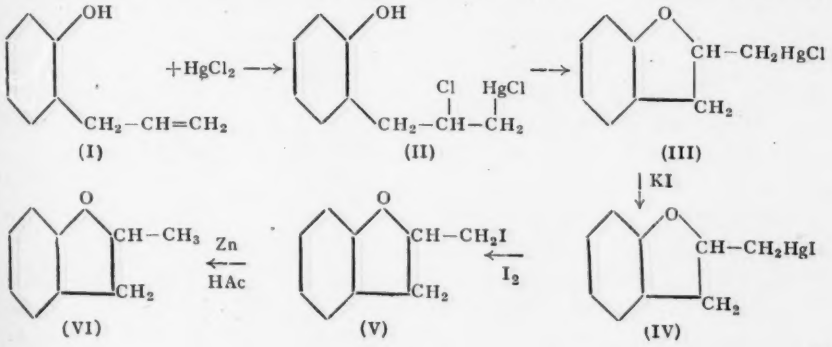
Received October 17, 1940

IN the previous papers[1,2] of this series the methods that have been employed for building up a fresh furan ring fused to the benzene nucleus of a coumarin structure have been discussed. Besides applying the best of these for the production of flavono-furans, a new method of effecting the synthesis of unsubstituted coumarino- and flavono-furan derivatives has also been explored. Another possible procedure of easily building up α-methyl-furan rings on coumarin and flavone ring systems has now been examined and the syntheses of the angular type of compounds are described in this paper. The method is essentially the same as that adopted by Adams *et al.*,[3] using *o*-allyl-phenol and mercuric chloride, though certain important modifications have been introduced with a view to simplify the procedure and improve the yields.

In their attempts to prepare acid stable organo-mercury compounds Adams *et al.*, examined the action of mercuric chloride and mercuric acetate on *o*-allyl-phenol. The products were found to be mercury derivatives of α-methyl-coumarans which were obviously transformation products of the initial addition of the mercury salts to the double bond of the allyl group.

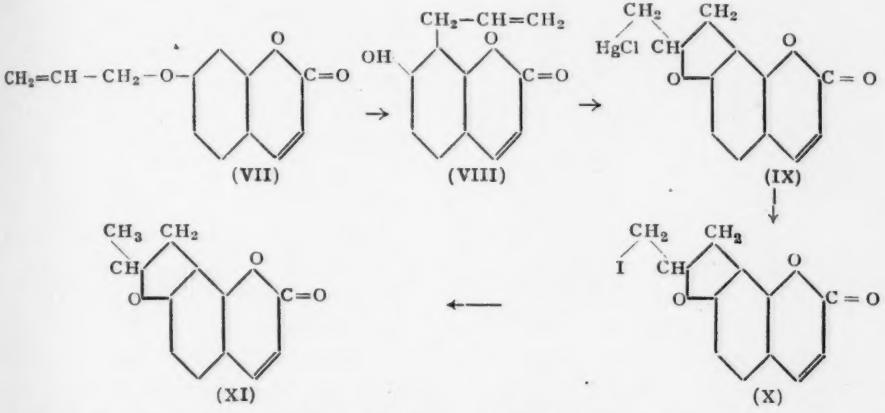


The positions of attack of the two parts of the addenda was inferred from analogy with similar additions (Markownikow's rule). The chloromercury compound (III) was found to undergo transformation readily into the iodomercury derivative (IV) by the action of potassium iodide and this could be converted into the corresponding iodo-compound (V). Further reduction with zinc and acetic acid gave rise to α-methyl-coumaran (VI).

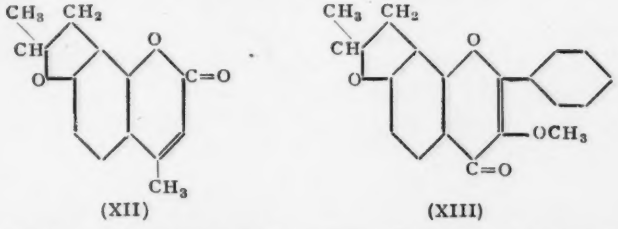
For purposes of the present investigation umbelliferone, 4-methyl-umbelliferone, and 3-methoxy-7-hydroxy-flavone have been employed as starting materials. Their allyl ethers undergo migration to form the corresponding allyl-phenols. The position taken up by the allyl group has been from close analogy assumed to be the 8-position. This point has been established by Baker and Lothian[4] in connection with 4-methyl-umbelliferone, and by Rangaswami and Seshadri[5] in connection with chromones and flavones. In regard to the best conditions for bringing about the Claisen migration, the work of Baker and Lothian may here be mentioned. 7-Allyloxy-4-methyl-coumarin was heated in an oil-bath. The migration was considered to be an exothermic reaction which started at 240°. After the bath had attained this temperature, the reaction was completed by cooling to 210° and maintaining this temperature for 1½ hours. But when this method was adopted in the present investigation, the product contained a good deal of resin and purification was very difficult. As a result of several experiments carried out by us under varying conditions of temperature and pressure, it was found that satisfactory yields could be obtained when the allyl ethers were heated under reduced pressure (20 mm.) at 195–200° for 1½ hours. In the preparation of 8-allyl-7-hydroxy-3-methoxy-flavones from 7-allyloxy-3-methoxy-flavone, a yield of 80% was obtained.

The action of mercuric chloride on the allyl compounds mentioned above takes place very easily in alcoholic solutions. In regard to their characterisation, estimation of mercury alone is not sufficient since in some cases no appreciable difference in the mercury content exists between simple addition products of type (II) and the further condensation product of type (III). Estimation of chlorine was found to be more useful for this purpose. That the ring closure takes place directly in all the cases examined has been established beyond doubt from analysis of carbon, halogen and mercury. Demercuration using hydrogen sulphide has been found to be useful in a large number of other compounds[6] studied previously in these laboratories. In the present set of compounds this method has not been successful since besides demercuration opening of the dihydrofuran ring also takes place. Though the method adopted by Adams *et al.*,[3] is quite good, the process could be simplified by using iodine and potassium iodide together instead of

employing them separately. By this means the preparation of iodomercurimethyl compounds as intermediates was avoided. For the final reduction of the iodine compounds zinc and acetic acid were used in the past. This has been found to be unsatisfactory for the present purpose as complete reduction could not be effected even after long treatment. This is partly due to the insolubility of the iodo-compounds in acetic acid. On the other hand using sodium and alcohol, the reaction proceeded smoothly and satisfactory yields of the α-methyl-dihydrofurans were obtained. The course of the reactions may be represented as below using the umbelliferone series as a representative case, the final product being coumarino-α-methyl-7 : 8-dihydrofuran (XI).



Similarly from 4-methyl-umbelliferone, 4-methyl-coumarino-α-methyl-7 : 8-dihydrofuran (XII) and from 7-hydroxy-3-methoxy-flavone, 3-methoxy-flavono-α-methyl-7 : 8-dihydrofuran (XIII) were obtained.



The dihydrofurans that have been prepared now and described in this paper are related to the simple coumarinofuran angelicin and the flavonofuran karanjin occurring in nature. On dehydrogenation they will yield α-methylhomologues of these naturally occurring compounds and this method

seems to open up possibilities of obtaining pyrono-furans easily and in good yield. Experiments on dehydrogenation are in progress.

Experimental

7-*Allyloxy-coumarin.*—Umbelliferone (8 g.) was dissolved in acetone (50 c.c.), allyl bromide (7 g.) and anhydrous potassium carbonate (15 g.) were added and the mixture was refluxed for 6 hours. After distilling off most of the acetone, the residue was treated with water and the resulting solid filtered and recrystallised from alcohol. It crystallised as prismatic needles melting at 79–80° C. Yield 90%. (Found: C, 71·2; H, 5·3. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%.)

8-*Allyl*-7-*hydroxy-coumarin.*—7-Allyloxy-coumarin (5 g.) was heated under reduced pressure (20 mm.) at 195–200° for 1½ hours. The product was then cooled and subjected to repeated crystallisations from alcohol. A pale yellow crystalline solid (tapering plates) was thus obtained melting at 162–63°. It gave a greenish blue fluorescence in dilute sodium hydroxide solution but no perceptible colour was obtained with ferric chloride. Yield 1 g. (Found: C, 71·4; H, 5·2. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%.)

Coumarino-α-chloromercurimethyl-7:8-*dihydrofuran.*—8-Allyl-umbelliferone (1 g.) dissolved in methylated spirits was mixed with a solution of mercuric chloride in the same solvent. Precipitation which commenced after 2 hours was complete within two days. The colourless substance which was obtained by filtration and washing with a little alcohol had the appearance of a microcrystalline powder and melted at 233–35° C. Since it was sparingly soluble, it was purified by repeatedly washing with hot alcohol. Yield 2 g. (Found: C, 32·8; Hg, 45·8; Cl, 7·8. $C_{12}H_9O_3$ HgCl requires C, 32·9; Hg, 45·9; Cl, 8·1. $C_{12}H_{10}O_3$ $HgCl_2$ requires C, 30·4; Hg, 42·4; Cl, 15·0 %.)

Coumarino-α-iodomethyl-7 : 8-*dihydrofuran.*—The above chloromercuri-compound (1 g.) was shaken with a fairly concentrated solution of iodine in potassium iodide (5 c.c.) with warming on a water-bath. Soon a distinct change in the nature of the solid was observed and about 15 minutes of this treatment was found to be enough for complete demercuration. The product was filtered and recrystallised from alcohol, when it was obtained as broad rectangular plates, melting at 168–69° C. The yield was almost quantitative. (Found: I, 38·4. $C_{12}H_9O_3I$ requires I, 38·7%.)

Coumarino-α-methyl-7 : 8-*dihydrofuran* (α-methyl-dihydroangelicin).—The above iodomethyl compound (0·4 g.) was dissolved in alcohol (10 c.c.) and small pieces of sodium (2 g.) were added one by one and kept pressed

to the bottom of the container by means of a glass rod in order to prevent the metal from floating to the top. After the reaction was over, the alcoholic solution was diluted with water, acidified and the resulting precipitate filtered. On recrystallisation from alcohol it was obtained as thin needles melting at 148–49° C. Yield 0·1 g. (Found: C, 71·2; H, 5·1. $C_{12}H_{10}O_3$ requires C, 71·3; H, 5·0%.) The molecular weight of the compound was determined by Rast's method and found to be 197 ($C_{12}H_{10}O_3 = 202$).

8-*Allyl*-4-*methyl-umbelliferone*.—It was prepared by subjecting 7-allyloxy-4-methyl-coumarin to Claisen migration under the modified conditions. The product was crystallised from alcohol when it melted at 193–94° C. (Baker and Lothian, m.p. 193–94°). Yield 25%.

4-*Methyl-coumarino-α-chloromercurimethyl*-7 : 8-*dihydrofuran* was readily obtained by means of the method already described. It crystallised from boiling alcohol as colourless short needles melting at 225–27° C. Yield 90%. (Found: Cl, 8·0. $C_{13}H_{11}O_3$ HgCl requires Cl, 7·9%. $C_{13}H_{12}O_3$ $HgCl_2$ requires Cl, 14·6%.)

4-*Methyl-coumarino-α-iodomethyl*-7 : 8-*dihydrofuran* which was prepared by the action of iodine in potassium iodide on the above chloromercuri-compound crystallised from alcohol as broad rectangular plates melting at 158–59° C. The yield was almost quantitative. (Found: I, 36·8. $C_{13}H_{11}O_3I$ requires I, 37·1%.)

4-*Methyl-coumarino-α-methyl*-7 : 8-*dihydrofuran* (α : 4-dimethyl-dihydro-angelicin).—The removal of iodine was effected by means of sodium and alcohol as already described. The product crystallised out of alcohol as thin rectangular plates melting at 182–83° C. Yield 25% on the weight of the iodine compound. (Found: C, 72·4; H, 5·4. $C_{13}H_{12}O_3$ requires C, 72·2; H, 5·6%.) The molecular weight by Rast's method was found to be 212 ($C_{13}H_{12}O_3 = 216$).

7-*Allyloxy*-3-*methoxy-flavone*.—7-Hydroxy-3-methoxy-flavone prepared by Allan and Robinson's method, was allylated as in the previous cases. The allyl ether when recrystallised from alcohol yielded colourless rhombic plates melting at 107–08° C. Yield was almost quantitative. (Found: C, 73·9; H, 5·0. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%.)

8-*Allyl*-7-*hydroxy*-3-*methoxy-flavone* was obtained by subjecting the above allyl ether to Claisen migration under reduced pressure (20 mm.). It was recrystallised from alcohol when it was obtained in the form of short needles melting at 243–44° C. Yield was 80% of the theoretical. On treatment with alkali the substance first dissolved giving an yellow solution but soon the

sodium salt precipitated out. It did not give any perceptible colour with ferric chloride but exhibited a greenish yellow fluorescence in sulphuric acid solution. (Found: C, 74·2; H, 5·3. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%.)

3-*Methoxy-flavono-α-iodomethyl*-7 : 8-*dihydrofuran*.—On treatment with mercuric chloride the above allyl-hydroxy-flavone gave the chloromercuri-compound which was yellow in colour. It did not give a definite melting point but decomposed on heating just above 200°. On treatment with iodine and potassium iodide it smoothly underwent conversion into the α-iodomethyl compound which was recrystallised from alcohol. It was obtained in the form of colourless long rectangular plates melting at 205–06°. (Found: I, 28·9. $C_{19}H_{15}O_4I$ requires I, 29·3%.)

3-*Methoxy-flavono-α-methyl*-7 : 8-*dihydrofuran* (α-methyl-dihydrokaranjin) was prepared by reduction of the iodine compound with sodium and alcohol in an yield of 40%. On recrystallisation from alcohol it was obtained as colourless thin rectangular plates melting at 133–34°. It was insoluble in cold as well as hot dilute sodium hydroxide and gave no colour with ferric chloride. (Found: C, 74·2; H, 5·3. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%.)

Summary

A fresh method for building up furan rings on to coumarin and flavone compounds has been studied. Starting with umbelliferone, 4-methyl-umbelliferone and 3-methoxy-7-hydroxy-flavone the corresponding angular α-methyl-dihydrofuran derivatives have been obtained. The 8-allyl compounds are first prepared and these are subjected successively to treatment with mercuric chloride, iodine in potassium iodide solution and sodium in alcohol.

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STUDIES IN CHLORAL AMIDES—PART VII

By (Late) N. W. Hirwe and P. Y. Kulkarni

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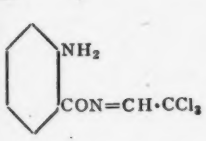
Received August 27, 1940

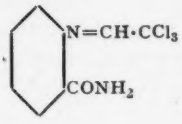
(Communicated by Prof. R. C. Shah, M.Sc., Ph.D., A.I.I.Sc.)

Aldol type condensation products ($RCO \cdot NH \cdot CH \cdot OH \cdot CCl_3$) of chloral and acid amides have long been known. The effect of the various* substituents in the benzene nucleus of benzamide on its condensation with chloral has been studied in this Laboratory. In this paper the condensations of chloral with anthranilamide, *o*-, *m*- and *p*-acylamido-benzamides and 5-bromo-2-acylamido-benzamides have been described with a view to study the effect of the nuclear substituents on the chloral condensations of these amides. The bromination of chloral-2-acetamido-benzamide also has been incidentally studied.

Anthranilamide on direct condensation with chloral gave a paste, from which no definite product could be isolated. The reaction appeared to be complex, probably due to the presence of the highly active amino group. However, anthranilamide hydrochloride condensed with chloral giving only one definite product. It formed a monoacetyl derivative but did not give a hydrochloride. It may have any of the following (I, II or III) constitutions.



I



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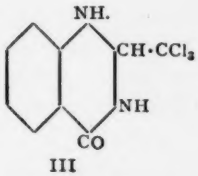

III

Constitution (I) is not likely, for the product gives neither the diazotisation reaction for the free amino group nor a salt with mineral acids. Constitution (II) could not be assigned, for the product is very stable towards hydrochloric acid. Such substances, containing the group $-N=CH \cdot CCl_3$, on boiling with a dilute mineral acid, hydrolyse to chloral and the corresponding amino compounds.[1] Constitution (III) containing a heterocyclic

* Hirwe and Rana, *Ber.*, 1939, **72**, 1346; Hirwe, (Miss) Gavankar and Patil, *Proc. Ind. Acad. Sci.*, (A), 1940, **11**, 512.

[1] *Cf.* Wheeler and co-workers, *J. Am. Chem. Soc.*, 1908, **30**, 136.

ring is the most probable one for the above product. Hirwe and (Miss) Gavankar (*Private communication*) have obtained a similar ring-closed compound, when they condensed chloral with 5-nitrosalicylamide. Parallel examples of direct ring formation are on record.[2]

2-Acetamido-benzamide, 3-acetamido-benzamide and 4-acetamido-benzamide, as also 2-benzamido-benzamide and 3-benzamido-benzamide condensed with chloral, when heated for a short time on a low flame; but 4-benzamido-benzamide required boiling for three hours to effect complete condensation. The *o*- and *m*-benzamido groups had nearly the same retarding influence as that of the *o*-, *m*- and *p*-acetamido groups but *p*-benzamido group had a much greater retarding influence. Thus the acylamido groups retarded the condensation of chloral with the amido group, as these amides condensed less readily with chloral than benzamide.

Unlike in salicylamide,[3] the presence of the additional negative 5-bromo radical in 5-bromo-2-acetamido-benzamide and 5-bromo-2-benzamido-benzamide did not exert an increased retarding influence on the chloral condensation of these amides, as these amides condensed with chloral in the usual way on boiling for a short time. Also the bromination product of chloral-2-acetamido-benzamide was found to be the usual 5-derivative and not the 3-derivative, as in chloral salicylamide,[4] showing that the *p*-directing influence of acetamido group is not sufficiently affected by the chloralamido group.

Experimental

1. *Condensation of Chloral with Anthranilamide.*—

2-*Trichloro-methyl*-4-*keto*-1 : 2-3 : 4-*tetrahydro-quinazoline.*—2-Amino-benzamide-hydrochloride (3 g.) and chloral (2 g.) were mixed in a tube fitted with an air condenser and heated on a water-bath at 60–70° C. for 30 minutes. On cooling, the reaction mixture was poured into water, when a granulated product separated out. Yield 50%. It crystallised in white needles from dilute alcohol, m.p. 202°. The product was soluble in acetic acid, acetone, ethyl alcohol, methyl alcohol and benzene. The product did not give colour test when diazotised and coupled with β-naphthol. The product was insoluble in dilute hydrochloric acid and caustic soda (10%).

It did not form a salt with hydrochloric acid and was stable towards concentrated hydrochloric acid at boiling temperature. (Found: N, 10·45; and Cl, 39·9. $C_9H_7N_2OCl_3$ requires N, 10·54; Cl, 40·1%.)

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[2] *Cf.* Keane and Nicholls, *J.C.S.*, 1907, **91**, 266; Hicks, *ibid.*, 1910, **97**, 1032.
[3] *Cf.* Hirwe and Rana, *Ber.*, 1939, **72**, 1346.
[4] *Cf.* Hirwe and Rana, *loc. cit.*

Acetyl Derivative.—The above condensation product of anthranilamide and chloral (1 g.) was dissolved in acetic anhydride with a drop of sulphuric acid in a test-tube fitted with an air condenser and was warmed on water-bath for two hours. The mixture was kept overnight and then poured into water, when a flocculent mass separated out. Yield 70%. It crystallised in small granules from dilute alcohol, m.p. 194–95°. (Found: Cl, 34·5. $C_{11}H_9N_2O_2Cl_3$ requires Cl, 34·6%.)

2. *Condensation of Chloral with* o-, m- *and* p-*Acetamido-benzamide*, o-, m- *and* m-*Benzamido-benzamide*, 5-*Bromo*-2-*acetamido-benzamide and* 5-*Bromo*-2-*benzamido-benazmide.*—

General Method of Condensation.—Amide (10 g.) and chloral (15 g.) were heated together in a flask fitted with an air condenser. The reaction progressed to completion vigorously within twenty minutes. To ensure completion of the reaction the reaction mixture was heated for two hours on a low flame. On cooling, it was poured into water and kept overnight, when a granulated mass separated out. The crude product was filtered and washed free from chloral. All the chloral amides were crystalline compounds and decomposed at the melting point into the corresponding amide and chloral. They were unstable towards alkalies at room temperature and towards sulphuric acid even below 10° C. All of them were soluble in alcohol, acetone, acetic acid and benzene, except chloral-4-benzamido-benzamide, which was sparingly soluble in acetone and acetic acid.

Chloral-2-*acetamido-benzamide.*—It crystallised from dilute alcohol in fine white needles, m.p. 172–73°. Yield 90%. (Found: C, 40·7; H, 3·6; N, 8·6; Cl, 32·6. $C_{11}H_{11}O_3N_2Cl_3$ requires C, 40·6; H, 3·4; N, 8·6; Cl, 32·7%.)

Chloral-3-*acetamido-benzamide.*—It crystallised from alcohol in fine granules, m.p. 164–65°. Yield 90%. (Found: C, 40·5; H, 3·4; N, 8·3; Cl, 32·7. $C_{11}H_{11}O_3N_2Cl_3$ requires C, 40·6; H, 3·4; N, 8·6; Cl, 32·7%.)

Chloral-4-*acetamido-benzamide.*—It crystallised from alcohol in fine granules, m.p. 259–60°. Yield 85%. (Found: C, 41·0; H, 3·6; N, 8·4; Cl, 32·8. $C_{11}H_{11}O_3N_2Cl_3$ requires C, 40·6; H, 3·4; N, 8·6; Cl, 32·7%.)

Chloral-2-*benzamido-benzamide.*—It crystallised from dilute alcohol in minute granules, m.p. 168–69° C. Yield 90%. (Found: C, 49·9; H, 3·5; N, 6·8; Cl, 27·6. $C_{16}H_{13}O_3N_2Cl_3$ requires C, 49·6; H, 3·4; N, 7·2; Cl, 27·5 %.)

Chloral-3-*benzamido-benzamide.*—It crystallised from alcohol in white shining needles, m.p. 232–33° C. Yield 90%. (Found: C, 49·5; H, 3·6;

N, 7·0; Cl, 27·5. $C_{16}H_{13}O_3N_2Cl_3$ requires C, 49·6; H, 3·4; N, 7·2; Cl, 27·5%.)

Chloral-4-benzamido-benzamide.—It crystallised from acetone in small granules, m.p. 212–13°. Yield 60%. (Found: N, 7·4; Cl, 27·2. $C_{16}H_{13}O_3N_2Cl_3$ requires N, 7·2; Cl, 27·5%.)

Chloral-5-bromo-2-acetamido-benzamide.—It crystallised from alcohol in fine granules, m.p. 171–72°. Yield 85%. [Found: N, 6·7; Halogen (1 Br + 3 Cl), 46·0. $C_{11}H_{10}O_3N_2Cl_3$ requires N, 6·9; Halogen (1 Br + 3 Cl), 46·1%.]

Chloral-5-bromo-2-benzamido-benzamide.—It crystallised from benzene, m.p. 171°. It was very unstable and decomposed partly during crystallization. Yield 75%. [Found: N, 6·17; Halogen (1 Br + 3 Cl), 39·6. $C_{16}H_{12}O_3N_2Br\ Cl_3$ requires N, 6·0; Halogen (1 Br + Cl 3), 40·0%.]

3. *Bromination of Chloral-2-acetamido-benzamide.*—

Bromine vapours (2·5 g.) were gradually aspirated through a solution of chloral-2-acetamido-benzamide (5 g.) in glacial acetic acid below 10° C. and kept overnight at room temperature. Part of the brominated compound was crystallised from the brominated solution and the remaining was recovered by dilution of the brominated solution. It recrystallised from dilute alcohol in needles, m.p. 172°. It did not show any lowering of temperature of m.p. when mixed with chloral-5-bromo-2-acetamido-benzamide. [Found: Halogen (1 Br + 3 Cl), 46·8; $C_{11}\ H_{10}O_3N_2BrCl_3$ requires Halogen, 46·1%.]

Hydrolysis

The brominated compound (1 g.) was mixed with 10 c.c. sodium hydroxide (10%) in a tube fitted with a condenser and gradually heated till the solution was clear. On cooling it was acidified with dilute acetic acid, filtered, washed and crystallised from dilute alchohol. It gave m.p. 298° when entered in the bath at 287° C. It showed no lowering of m.p. when mixed with an authentic sample of 2-methyl-4-keto-6-bromo-3: 4-dihydroquinazoline.[5]

Thanks are due to Prof. R. C. Shah for his interest in this work.

[5] *Cf.* Bogert and Hand, *J. Am. Chem. Soc.*, **28**, 101.

ELECTROLYTIC RESTORATION OF BRONZE STATUES AND INSCRIBED COPPER-PLATES

By S. Paramasivan

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Received December 5, 1940

1. *Introduction*

The electrolytic process for the restoration of ancient bronzes, which is the reversal of the process of corrosion,[1] was first suggested by Finkener,[2] Ch. Frisch,[3] François Margival[4] and Francesco Rocchi.[5] But these suggestions were not put to much practical use. It was Colin G. Fink,[6] who worked out the experimental details for the first time and recommended its adoption on an extensive scale for the restoration of ancient bronzes in the Metropolitan Museum of Art of New York in preference to the older chemical methods advocated by Dr. Alexander Scott[7] of the British Museum. The electrolytic method was so startling in its effects that the Field Museum of Natural History,[8] Chicago, Museum of the University of Pennsylvania,[9] Fogg Art Museum of the Harvard University, Cambridge, Mass., and other American Museums have been regularly adopting it.

But the electrolytic restoration of Bronzes was popular only in America, and has been exclusively confined to the treatment of small bronze objects measuring about one foot at the most in extreme cases. Recently, the process has been extended in the Madras Government Museum for the restoration of ancient bronze statues which measure about 4 feet in height. Thus these bronzes are much larger than the ones ever treated elsewhere. The process has also been successfully adopted for the restoration of inscribed and heavily corroded copper-plates, probably for the first time.

2. *Ancient Bronzes in Madras Museum*

The Madras Government Museum has the richest collection of ancient bronzes in India. They are of wonderful artistic workmanship and some of them are the largest and the most famous throughout the world. Many of them are treasure trove finds. Through long burial in the earth, they have become covered with thick crusts which are composed of the products of corrosion. The crust not only hides the details of artistic workmanship, but frequently eats into the bronze, thereby causing considerable damage

to it. Thus the main problems with these bronzes are, (1) to remove the disfiguring incrustations which conceal the decorative details, (2) to restore to the object its original appearance and (3) to eliminate the corrosive substances which cause rapid disintegration and thus to assure the permanence of the valuable exhibit. These have been effected by the electrolytic process.

3. Chemical Composition of the Bronzes

The collection of bronze statues in the Madras Museum date from about the ninth century A.D. down to modern times. Bronzes belonging to various periods were selected at random and drillings taken from their pedestals or other unimportant portions were analysed. The results of analysis were as follows:—

Chemical Analyses (*Per cent.*)

	10–11th century A.D.	13th century A.D.	15th century A.D.	17th century A.D.
Cu ..	86·88	91·05	96·29	91·25
Sn ..	10·44	2·86	2·58	6·66
As ..	Tr	Tr	Tr	Tr
Pb ..	1·48	6·09	1·09	2·02
Fe ..	1·19	Tr	0·06	0·07

The results of chemical analysis clearly show that Indian bronzes are rich in copper and that tin has been specially added to harden the alloy. In the case of the thirteenth century bronze, lead* has been purposely added, probably with the object of hardening the alloy. The same is true of iron in the tenth-eleventh century bronze.

4. Composition of Corrosion Products

The composition of the corrosion products of museum exhibits have been fully discussed by Rathgen.[10] It is not, however, an easy matter to collect samples of corrosion products from the valuable bronze collections of various periods exhibited in the Madras Museum, for purposes of analysis. Even if they are available, the results of analysis are not of importance for comparison, especially when corrosion has not taken place under identical conditions. The following however are the results of analysis of typical corrosion products from a bronze belonging to the ninth century A.D.:—

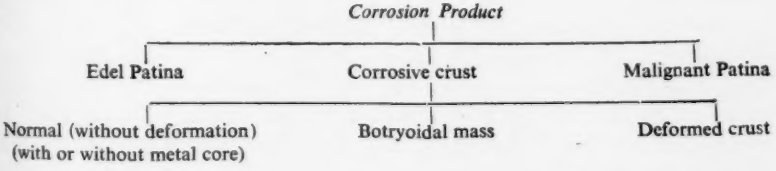
* Lead occurs also in early Babylonian and Egyptian bronzes.

Chemical Analysis (*Per cent.*)

	Bronze	Patina
Copper	83·39	76·16
Tin	16·61	15·09
Lead	Tr	Tr
Arsenic	Tr	—
Iron	Tr	0·09
Water		1·23
Carbon dioxide		1·75
Sulphuric anhydride, SO_3 ..		Tr
Chlorine		Tr
Oxygen		5·52
Lime, CaO		0·14

In some of the bronze statues, the patina invariably holds a large proportion of sand through long burial in the earth. Thus the corroding agents ever present in moist soils have converted the copper and tin into mineral compounds such as oxides, chlorides, sulphates and carbonates (malachite and azurite). With the Madras Museum specimens, the corrosion has not gone deep and there is still sufficient metal left.

The bronze statues in the Madras Museum have been subjected to different degrees of disintegration. The crusts thus formed as a result of corrosion can be classified thus:—



(*i*) A few of the bronzes are covered with a thin transparent coat of minerals of pleasing colour and of enamel-like appearance, which gives an air of antiquity to the bronze. This coating is called *Edel patina*.[11] The metal surface under it is quite smooth. The *Edel patina* does not obscure the details of workmanship. On the other hand, it protects it.

(*ii*) In some cases, the surface of the bronze is covered with a thick non-translucent crust, which is rough and obscures the decorative details. The crust might be quite normal, or it might be a botryoidal mass of malachite and azurite or it might be outwardly deformed. When the crust is normal, the metal under it is perfect. At times it might be roughened and pitted. When the crust is of a botryoidal mass, the surface under it is always roughened and pitted. Some of the bronzes are heavily encrusted and outwardly deformed, the latter being confined to the crust alone. Ordinarily bronze statues seem to resist the distorting forces as the excess material, in the form of oxidation products, migrates outwards and is deposited on the outer crust.

In all the cases, where the surface of the bronze is not roughened or pitted, the oxide of copper which replaces the original metal surface retains the details of that surface.

(*iii*) Some of the bronzes have *Malignant patina* on them. If unchecked, the smallest patch of it will destroy the entire bronze. It is erratic in its action. A patch of it, not larger than a pin's head, may remain passive for years and then, for no apparent reason, suddenly become active. *Malignant patina* is due to the presence of copper salts[12] such as the chloride or the sulphate which adheres to the surface and is occluded in the pores of the corroded bronze. They continue the destructive action indefinitely even after the bronze has been removed from the primary source of trouble.

5. *Process of Corrosion*

The crusts or the products of corrosion of a bronze are due to electrochemical action[13] which in turn, depends upon various factors such as the amount of moisture and the salinity of the soil in which the statues have long buried. It is also influenced by the duplex structure of the copper alloy which contains very slight impurities of more or less noble metals. These impurities set up many local miniature electrolytic cells on the metallic surface. The salts in the ground water serve as electrolytes. Inequalities in the concentration of the salts and the amount of oxygen present in it give rise to differences in the electrolytic potentials. They result in the transport of the metallic ions from one local area to another. On some of these local areas (anodic), the copper is attacked by the salt and a soluble copper salt is formed. On other areas, which are cathodic, alkali accumulates, and the copper is little affected. The action of the salt and oxygen can be properly expressed thus:—

$$Cu + 2\,NaCl + H_2O + O \rightarrow \underset{\text{Anodic}}{CuCl_2} + \underset{\text{Cathodic}}{2\,NaOH}$$

This reaction takes place only when conditions are such as will tend to cause a difference of potential between closely adjacent local areas on the surface of copper. A similar local electrolytic action gives rise to pitting on the surface of the bronze. Such differences of potential between the different parts of the metal might be as much due to physical or chemical variations in the metal itself, *viz.*, local strains, segregations of impurities, presence of second metal phase, as to variations external to the metal, such as differences of oxygen or metal ion concentration.[14]

The actual rate of corrosion in any particular case is determined by various factors in the soil, the interaction of which makes the subject exceedingly complicated. Some of the factors which operate on the bronzes while lying buried under the earth are as follows:—

Relating to metal

1. Electrode potential.
2. State of aggregation.
3. Presence of internal stresses.
4. Overpotential.
5. Nature of concentration of metals in solid solutions.
6. Nature, amount and distribution of second phase.
7. Chemical reactivity.

Relating to external conditions

8. Temperature.
9. Pressure of oxygen.
10. Rate of supply and distribution of oxygen.
11. H-ion concentration.
12. Nature and distribution of corrosion products.
13. Conductivity of the liquid.
14. Metal ion concentration.
15. Specific nature of ions present.

With treasure trove finds which have been lying buried in moist soils containing water alone or salt solution, (12) becomes very important since the films and mounds of corrosion products might form at the metal surface and affect other factors in a complicated manner.

6. *Electrolytic Restoration*

Without any preliminary treatment, the corroded bronze statue is placed in an iron tank or cell and insulated from it by porcelain insulators. The cell contains a 2% solution of sodium hydroxide. A current of electricity is allowed to pass through the cell, the bronze acting as the cathode and the iron tank as the anode. The process consists in the electrolytic decomposition of the sodium hydroxide and the evolution of hydrogen at the cathode, which reduces the crust to finely devided or spongy copper, which can be brushed off, with the result that the decorative details are exposed.

Before starting the electrolytic reduction of specially valuable and heavily corroded bronzes, radiographs of them are taken in order to find out the extent of the corrosion, the nature of the precautions to be taken in the course of electrolytic reduction and the final result to be expected.

7. *Apparatus at the Madras Museum*

The apparatus used for the electrolytic restoration of heavy bronzes is not unlike that used for electroplating on a large scale. It consists of a 7 kilowatt motor generator set capable of generating up to 60 amps. at any voltage ranging from 0 to 110. In addition, there are means of measuring and controlling voltage and the current supply. There are also electrolytic cells to conduct the reduction in.

Current Supply.—The motor generator set is fed by 440 volts D.C. power. Its output is a direct current, which may be regulated up to 110 volts or 60 amps., provided its maximum capacity of 7 kilowatts is not exceeded. The voltage is regulated by a rheostat in the field winding of the generator. All the controls for the motor and the generator are on a marble-panelled switch board.

There are three parallel circuits leading from the control switch board to a separate room in which the electrolytic cells are housed. The electrolytic reactions in the cells can be independently controlled from the switch board. The current in the first circuit can be varied from 0 to 60 amps. by a control rheostat joined in series. The current passing through the second and the third circuits can be similarly varied from 0 to 20 amps. and 0 to 5 amps. respectively by suitable rheostats. In this equipment, the output under constant load does not fluctuate, except when the voltage is low, namely 0 to 30 volts. If the generator is to supply current at low voltage, the field rheostat is to be constantly adjusted to maintain the same current strength.

There are other sources of current supply such as utilising the 220 volts D.C. power line with suitable resistance lamps to reduce the voltage. In view of the experiences of American museums even with small bronzes, such equipments were found to be quite unsuitable for the restoration of large objects. Even storage cells were unsuitable. The motor generator has been found to be more useful from the point of view of its ease of operation and control and freedom from trouble.

Current Control.—The control panel has three ammeters respectively in the 0–60 amps., 0–20 amps., and 0–5 amps. circuits. In the first, readings can be adjusted correct to 1 amp. from 20–60 amps. This circuit is operated

only when the objects which require more than 20 amps. are to be restored. In the second circuit, the current strength can be adjusted correct to 0·5 amps. from 5–20 amps. This circuit is intended for the restoration of those objects which require more than 5 amps. In the third circuit, the amperage can be adjusted correct to 0·05 amp. and from 1–5 amps. and is specially used for the restoration of objects requiring more than 1 amp. It is only very rarely that objects requiring less than 1 amp. have to be restored. In such cases, readings correct to 0·05 amp. from 0–1 amp. can be obtained with another rheostat having a maximum resistance of 2000 ohms, and a current rating of 1 amp. A double throw knife switch is introduced in the 0–5 amps. circuit by which connection can be made either with the 0–5 amps. circuit or with a fourth circuit in which the current can be varied from 0–1 amp. To guard against damage from short circuits, fuses for the different circuits are provided in the switch board itself.

Measuring Instruments.—The effectiveness of the treatment and the safety of the specimens depend upon accurate knowledge and control of the current strength during electrolysis. For this purpose, well calibrated ammeters and voltmeters are provided in the switch board. The instruments are permanently in circuit. The voltage at the electrodes in the cells is determined by a separate portable Weston-type voltmeter.

The computation of the proper current strength to be used with each object is very important. Too heavy a current might result in too much gassing at the electrodes which might blast away the corrosive crust, thereby damaging the bronzes. It has been estimated that the current density at the cathode should always be from 1–5 amps. per sq. ft. With many objects, it is about 2 amps. per sq. ft. Where there is too much gassing at the cathode, the current density is even less. The voltage is kept low, preferably at about 10 volts. But if the crust offers resistance to the passage of current, the voltage is much higher, going up to about 110 volts in the initial stages.

The computation of the area of the cathode surface in order to determine the necessary current strength is an easy matter.[13]

Electrolytic Cells.—The weight and the size of the specimens preclude the use of electrolytic cells of glass or earthenware as in American museums. In the early stages of the eletrolytic work in the Madras Museum, paraffined wooden cells were used with an iron wire-gauze closely touching the inner walls acting as the anode. On account of troubles through leakage, they have now been discontinued. At present cylindrical iron tanks with welded joints have been substituted with success. Nothing that has been

tinned, galvanised, soldered or brazed can be used because of the secondary electrolytic action through formation of miniature cells.

Electrolyte.—The electrolyte used is a 2% solution of caustic soda. Commercial grade of caustic soda in flakes has been used. The avidity with which the substance absorbs moisture and carbon dioxide from air makes it necessary to observe certain precautions when storing or handling the substance. It is purchased in 1 and 5 lbs. tin containers. If the caustic soda is damp or in lumps, it is rejected lest the carbonate present in it should damage the valuable bronze.

For preparing the 2% solution of caustic soda, the following procedure is adopted. The cell is filled with water so as just to cover the top of the statue placed in it, and the level of the water marked. The statue is taken out of the cell and the level of water marked again. From the internal dimensions of the cylindrical cell and the difference in the two water levels, the volume is calculated in c.c.'s and this is numerically equivalent to the weight of water in grams. The amount of caustic soda needed will be just 2% of this.

The statue is now placed in the cell and insulated from it by porcelain cable insulators. After making the necessary electrical contacts, the cell is now filled with water so that only about four-fifths of the bronze is immersed in it. The requisite quantity of caustic soda is quickly weighed and separately dissolved in minimum quantity of water and poured into the cell, and the contents stirred. Water is then added to the cell till the bronze is just immersed. The specific gravity of this solution is 1·0207. As the commercial grade of caustic soda is not pure, the solution is slightly understrength, which does not affect the result. But if the strength is kept above 2%, damage will result to the bronzes during electrolysis.

Electrodes.—Formerly when wooden cells were used, anodes were cut out of wire-gauze and laid against the inner vertical wall of the cell, and then clamped. At present, the iron tank, insulated from the ground and from the bronze (cathode) by porcelain cable insulators, acts as the anode. It has a binding block of brass permanently clamped to the rim through which electrical connections are made from the switch board. These iron cells can be used over and over again. The cells in the Madras Museum have been in regular use for the last seven years, and are likely to last for many years more.

It has been found that the farther the anode is from the cathode, the more regular is the electrolytic reduction. This fact is always borne in mind when arranging the cathode in the cell. The bronze statue which stands

upright in the cell acts as the cathode and is clamped to a special stand through which proper electrical contacts are maintained. The weight of the entire bronze pressing upon the brass stand aids the maintenance of proper electrical contacts.

Objects in almost identical state of corrosion and measuring alike are clamped together and restored simultaneously in the same cell.

In the case of inscribed copper-plates, they are suspended in the electrolyte with two anodes (iron wire-gauze) suspended on either side of it. The anodes exactly resemble the cathode in shape.

A serious difficulty is encountered in the restoration of the inner walls of the base of the pedestal. The base always encloses air and is not filled with the electrolyte. Further the base of the brass stand completely covers the base of the pedestal, thereby preventing the electroyltic reduction. In such cases, a hole is drilled through the top of the pedestal which enables the enclosed air to escape and the electrolyte to fill the hollow. Further, a circle measuring about 4 inches in diameter is cut through the base of the stand, whereby the electrolytic action between the inner wall of the pedestal acting as the cathode and the bottom of the cell acting as the anode is not prevented.

In the case of heavily corroded bronzes, which are mostly small, the electrical connections are made by wrapping an annealed copper wire around the specimen in a close coil of three to six turns. When the specimen is entirely composed of earthy matter with high resistance, the wire is attached in the usual way and is carried in a loose spiral over the entire length of the specimen for the purpose of providing a larger contact surface. When the crust is thick it may happen that the crumbling of the coating during the treatment may release specimens which are mere shapeless concretions under such conditions, they are wrapped and tied with the wire much as a parcel is tied with a string.

Duration of Treatment.—The reduction of a thin crust 2 to 3 mm. in thickness usually requires 3 or 4 days. Bronzes with crusts varying from 3 to 6 mm. in thickness usually require 3 to 6 months of electrolytic treatment. The use of too strong an electrolyte or too high a current density or voltage causes excessive gassing at the electrode, and this gives rise to warping and disintegration, unless there is a strong metallic core. Thus with extremely corroded bronzes, where there is gassing even at low current density, the strength of the current has to be lowered still, in which case, the duration of treatment is correspondingly increased.

The metal compounds in the crust are slowly reduced back to metal and on further electrolysis, the finely divided metal becomes more and more compact. If this stage is desired, then the duration of treatment is correspondingly increased.

In the Madras Museum, the electrolytic plant is in operation for six hours a day and for 6 days in the week. The completion of the treatment is indicated by the gassing at the cathode even at low current density.

Results of Electrolytic Treatment.—The results of the electrolytic treatment of bronze statues can be set down thus:—

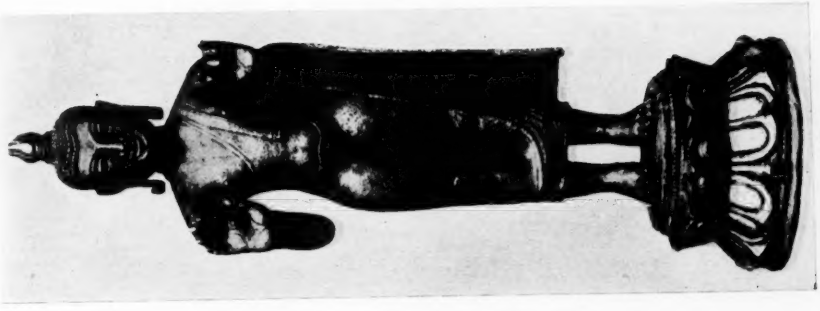
Nature of the crust	Results of treatment
1. Edel Patina	No treatment except when associated with destructive salts like the chloride or the sulphate. Where the surface under the patina is roughened or pitted by corrosive salts, the surface cannot be improved by treatment.
2. Malignant Patina	Good results.
3. Thick crusts obscuring details:—	
(*a*) Normal (with or without metal core)	Good results.
(*b*) Botryoidal Mass	Surface appears badly corroded after treatment.
(*c*) Deformed crust	Good results if the specimen is not very thin.

Record of Results.—The results of the electrolytic treatment are recorded as follows:—

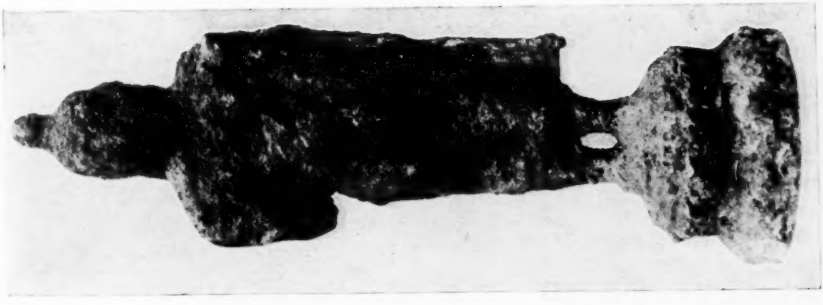
TABLE I

1 Serial No.	2 Catalogue No.	3 Dimensions	4 Weight		5 Appearance		6 Surface (area)	7 Voltage
			Before	After	Before	After		

8 Amperage	9 Strength of Electrolyte		10 Duration of treatment	11 Energy consumed	12 REMARKS
	Before	After			



After



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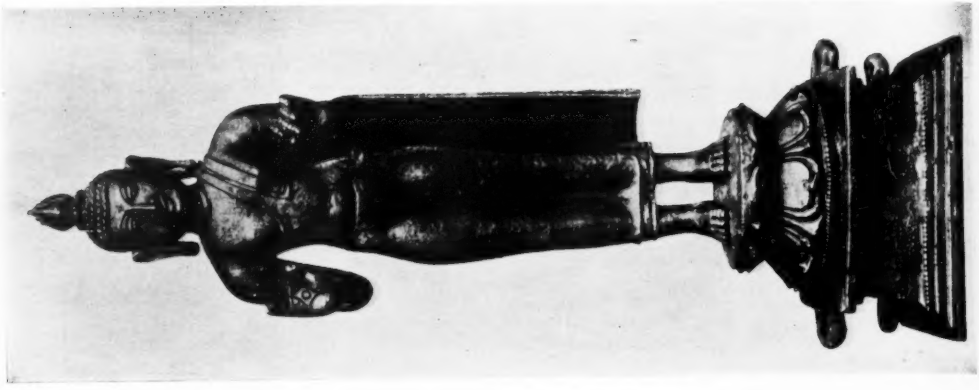
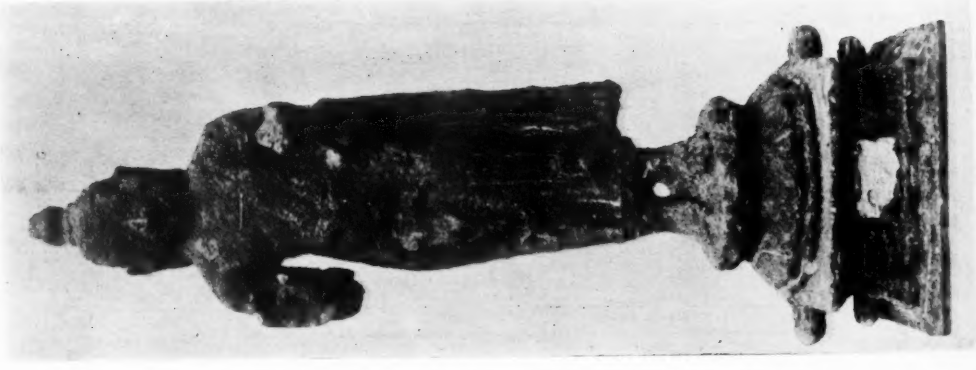


After



Before

After

Before

After

Before

After

Before

TABLE II

1 Serial No.	2 Date	3 Voltage	4 Amperage	5 Metre Reading		6 No. of units	7 REMARKS
				Initial	Final		

In conclusion, the author desires to express his thanks to Prof. Erlam Smith who suggested the problem to him and to Dr. F. H. Gravely for giving him the necessary facilities for carrying out the work.

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RELATIVE INTENSITIES OF STOKES AND ANTI-STOKES RAMAN LINES IN CRYSTALS

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Received November 18, 1940

(Communicated by Prof. S. Bhagavantam)

1. Introduction

The existence of the anti-Stokes lines in the Raman spectrum of a substance proves that, at ordinary temperatures, there will be some oscillators at a higher energy level than the normal and that the incident light induces a return of these to the normal state. Raman and Krishnan[1] showed that the relative intensities of the Stokes ($\nu - \nu_{mn}$) and the anti-Stokes ($\nu + \nu_{mn}$) lines, ν being the frequency of the incident light and ν_{mn} the transition frequency, are given by the relation $e^{-\frac{h\nu_{mn}}{kT}}$ where h is the Planck-constant, k is the Boltzmann-constant per molecule and T is the absolute temperature. Landsberg and Mandelstam[2], Tamm[3] and Ornstein and Rekveld[4] obtained a slightly modified expression, namely, $\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 e^{-\frac{h\nu_{mn}}{kT}}$ for this ratio. Placzek[5] considered the effect of absorption bands on this ratio and obtained an expression which may be shown to reduce to the above one, if the substance has no absorption bands in or near the region of investigation.

Considerable amount of work has been done by Ornstein and Rekveld[6] and Sirkar[7] in respect of the ratio of intensities between Stokes and anti-Stokes lines in liquids. The measurements of Ornstein and Rekveld in CCl_4 agree with the ordinary Boltzmann distribution function $e^{-\frac{h\nu_{mn}}{kT}}$ while those of Sirkar in the same liquid are in conformity with the modified formula $\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 e^{-\frac{h\nu_{mn}}{kT}}$. Landsberg and Mandelstam made some estimates of the above ratio in quartz at different temperatures and showed that the behaviour of the Stokes and anti-Stokes Raman lines was in conformity with the requirements of the ordinary Boltzmann distribution function. Ornstein and Went[8] determined the ratio of the Stokes and anti-Stokes lines in the Raman spectra of quartz and calcite. Their results, which are confined to the 465 line only in the case of quartz, are in good agreement with those calculated

on the basis of the modified expression while discrepancies are found in the case of calcite. In view of these discrepancies, it is proposed to study the cases of calcite and quartz in this paper.

2. *Experimental Details*

Light from a 6-inch quartz mercury arc lamp is condensed by means of an 8-inch glass condenser on to one face of the crystal and the scattered light emerging out of one of the other faces of the crystal is focussed on the slit of a two-prism glass spectrograph of high light gathering power with a suitable lens. In both the cases of calcite and quartz, cut and polished crystals of appreciable size (one-inch cubes) have been used and with suitable precautions, which are usually employed for obtaining good Raman spectra, intense and clear spectrograms showing the Stokes and the anti-Stokes lines have been obtained.

The plates are run through a Moll microphotometer and the densities of the various lines are obtained in the usual way. A set of intensity marks is recorded on each plate by the method of varying slit widths using the continuous radiation emitted by a standard quartz globe tungsten ribbon lamp as the source. A steady current of 15·1 amperes is maintained in the lamp in both the cases by feeding it from a battery of 220 volts. The colour temperature T of the lamp corresponding to the current drawn is given by the makers as 2695 and the radiation is assumed to obey Wien's law $E_\lambda = A\lambda^{-5}e^{-c_2/T\lambda}$ where $c_2 = 1{\cdot}432$, $T = 2695$ and A is a constant. The density at any desired wave-length is obtained for each of the intensity marks by running the plate through the microphotometer under the same conditions as above and the corresponding intensities are taken as proportional to the respective slit widths. In this way, the density-log intensity curves are drawn for each wave-length at which the various Raman lines that are to be compared with each other appear. The intensity of any line as a fraction of the standard radiation having the same wave-length as the line itself is easily read from the above curves and the relative intensities of the various Stokes and anti-Stokes lines are then computed from a knowledge of the energy distribution in the radiation emitted by the lamp. It may easily be seen that this procedure totally eliminates the error due to variations in the photographic sensitivity of the plate in different regions of the spectrum. Since the crystals are not very large and since they are perfectly colourless, no corrections need be made on the score of absorption by the crystal itself. This correction will, however, be of importance only in the case of long columns of liquid.

A few remarks may be made here on the question of measuring the peak intensities of the lines in preference to the integrated intensities or *vice versa*. This point is of special importance when we compare the intensities of different lines having different breadths or the intensities of the same line at different temperatures when the sharpness of the line in question changes with temperature. Since, in this investigation, we are comparing the intensity of a Stokes line with that of the corresponding anti-Stokes line, it is immaterial whether we measure the peak intensities or the integrated intensities because the Stokes lines have the same breadth characters as those possessed by the corresponding anti-Stokes lines. Accordingly, in the present paper, only the peak intensities are measured and compared.

3. *Results and Discussion*

The ratio of intensities between the Stokes and anti-Stokes lines in calcite and quartz obtained by the author are given in the last column of the following tables.

TABLE I

Calcite

Temperature	ν_{mn} cm^{-1}	Excitation A.U.	$e^{\frac{h\nu_{mn}}{kT}}$	$\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}$	$\frac{I_S}{I_{A.S.}}$ Observed
303° K.	155	4358	2·08	1·97	1·93
		4046	2·08	1·98	1·86
	280	4358	3·77	3·42	3·32
		4046	3·77	3·44	3·53

TABLE II

Quartz

Temperature	ν_{mn} cm^{-1}	Excitation A.U.	$e^{\frac{h\nu_{mn}}{kT}}$	$\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}$	$\frac{I_S}{I_{A.S.}}$ Observed
303° K.	465	4358	9·04	7·69	7·53
	127	4046	1·82	1·75	1·67

The values given in the last three columns of both the tables clearly reveal that the observed values of $\frac{I_S}{I_{A.S.}}$ agree more closely with the expression

$\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 \frac{h\nu_{mn}}{e^{\frac{h\nu_{mn}}{kT}}}$ than with $e^{\frac{h\nu_{mn}}{kT}}$ alone. Especially the ratios in the case of ν_{mn} 280 in calcite and of ν_{mn} 465 in quartz serve as deciding tests in favour of the former, the discrepancies between the observed results and those deduced on the basis of the latter expression being quite large in comparison with the possible experimental errors.

4. *Summary*

The ratios of intensities of various Stokes and anti-Stokes lines in the Raman spectra of calcite and quartz have been determined and the observed values are in better agreement with the values calculated on the basis of the expression $\left(\frac{\nu-\nu_{mn}}{\nu+\nu_{mn}}\right)^4 e^{\frac{h\nu_{mn}}{kT}}$ than with $e^{\frac{h\nu_{mn}}{kT}}$ alone.

In conclusion, the author desires to express his grateful thanks to Prof. S. Bhagavantam for his keen interest during the progress of this work.

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THE EFFECT OF UNSATURATED CHROMOPHORES ON PYRONINE DYESTUFFS

Part II. Dyes obtained from Maleic and Succinic Acids

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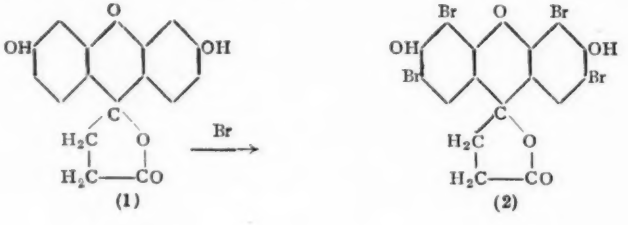
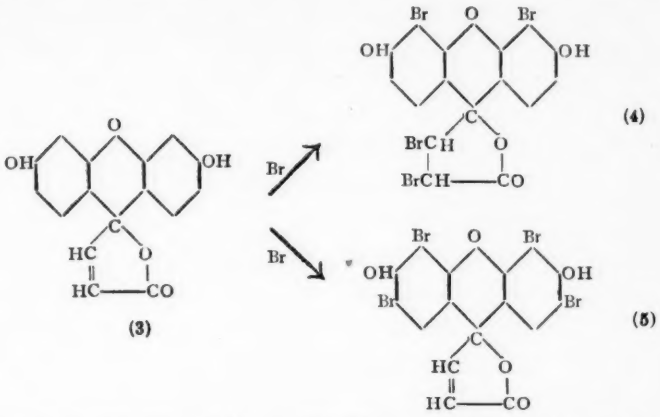
Received September 30, 1940
(Communicated by Dr. Satya Prakash, D.Sc., F.A.Sc.)

The effect of unsaturation in the pyronine type of dyestuffs has been studied in the first part of the series,[1] where a comparative study of the dyes obtained from aconitic and tricarballylic acids was made. In the present communication a further study is made from the same point of view of the dyes obtained by condensing various aromatic hydroxy and amino compounds with maleic acid, which are directly compared with the analogous dyes obtained from succinic acid, the saturated acid corresponding to maleic acid. A study of the eosine like compounds of the typical dyestuff of these series gave some interesting results. A few of the condensation products of both maleic[2] and succinic[3] acids with aromatic hydroxy compounds and of the latter acid with a few aromatic amino compounds have already been prepared but no comparative study of the dyestuffs thus obtained has so far been made. Workers in this field have obtained an eosine-like compound by brominating resorcinol-succinein but attempts[4] to prepare corresponding eosine-like compound from resorcinol-malein have been unsuccessful. In the present case a bromoderivative has been obtained from resorcinol-malein. Examination of the structure of the two typical compounds of each series reveals that whereas there is only one possible position the bromine atoms can occupy in the case of resorcinol-succinein, there are two possibilities in the case of resorcinol-malein.

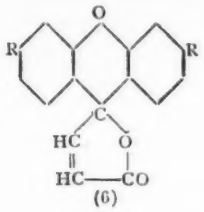


(1) (2)

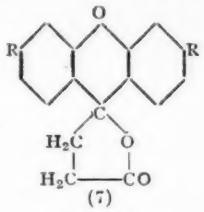


In (1) bromine can occupy by substitution the free positions in the two benzene nuclei but in (3) it can also be added to the double bond (just as maleic anhydride forms on bromination dibromosuccinic anhydride A Pictet, *Ber.*, 1881, **13**, 1669) and the remaining two atoms could occupy two of the positions in the benzene nuclei. It is obvious that these two possibilities in the case of brominated resorcinol-malein would not have arisen if the compound had taken up as was expected six atoms of bromine. But the results of repeated estimations of bromine in the compound by the method of Paria and Schiff indicate that like resorcinol-succinein, resorcinol-malein also takes up only four atoms of bromine. Thus to ascertain as to which of the two structures (4) or (5) represent the correct formula of the tetrabromoresorcinol-malein, brominated succinic acids were employed as starting material. Both mono- and di-bromosuccinic acids condense with resorcinol, without any condensing agent. It indicates that on heating both the bromoacids lose hydrogen bromide and form maleic and acetylene-di-carboxylic acids which get condensed with aromatic hydroxy and amino compounds in presence of liberated hydrogen bromide acting as condensing agent giving the corresponding fluoresceins and rhodamines which do not contain any bromine in the molecule. In both the cases the brominated resorcinol compounds contain only four atoms of bromine in the aromatic portion of the molecule. Fumaric acid also gives condensation products identical to maleic acid because on heating it changes to maleic anhydride.

The dyestuffs of these series tenaciously hold one molecule of water which is removed only by heating for about six to seven hours in the air oven. They have the general formulæ (6) and (7) similar to those in the case of aconiteins and tricarballyleins.



(6)
Malein



(7)
Succineins

The absorption maxima of the dyestuffs given in the table at the end of the paper clearly show that unsaturation in the molecule considerably enhances the intensity of the colour.

Experimental

Phenol-malein.—A mixture of 3 grams of maleic acid and 5 grams of phenol was heated in an oil bath at 125–35° C. for about ten hours with a few drops of concentrated sulphuric acid. The melt which solidified on cooling was freed from excess of phenol by steam distillation and filtered. The precipitate was extracted with dilute ammonia; from the extract the dyestuff was precipitated by the cautious addition of dilute hydrochloric acid, and was further purified by boiling in alcohol with animal charcoal, filtering and precipitating by cautiously diluting the alcohol and adding a little of hydrochloric acid. The purified dyestuff which is a light-brown powder, dissolves in ethyl and methyl alcohols with brown colour and in acetone with a deep reddish brown colour and was insoluble in chloroform, benzene and petroleum ether. Addition of alkali produces bright pink colour. It blackens at 170° C. and melts at 195° C. (Found: C, 71·53%; H, 4·64%. $C_{16}H_{12}O_4$ requires C, 71·64%; H, 4·47%.)

Catechol-malein.—A mixture of 3 grams of maleic acid and 6 grams of catechol was heated for twelve hours at a temperature of 120-30° C. in an oil bath with a long air condenser and about 5 c.c. of tin tetrachloride added. The melt which on cooling got solidified was boiled with water in order to remove excess of tin tetrachloride and filtered. The violet coloured residue which was the tin salt of the dyestuff was suspended in alcohol and a slow current of hydrogen sulphide was passed. Tin sulphide got precipitated and the dyestuff went down in solution. When all the tin salt was completely decomposed, tin sulphide was filtered off and the dyestuff precipitated from the filtrate by diluting with water and boiling off sulphuretted hydrogen, cooling and adding a few drops of hydrochloric acid. It was further purified by boiling with animal charcoal in alcohol and reprecipitating as before. The purified dyestuff which is a black powder dissolves in ethyl and methyl

alcohols with a chocolate-brown colour which deepens in acetone and is insoluble in chloroform, benzene and petroleum ether. Addition of alkali produces transient deep emerald green colour, m.p. 148° C. (Found: C, 67·53%; H, 4·01%. $C_{16}H_{10}O_5$ requires C, 68·06%; H, 3·54%.)

Pyrogallol-malein.—A mixture of 4 grams of maleic acid and 9 grams of pyrogallol was heated on the oil bath with a few drops of concentrated sulphuric acid at a temperature of 150–55° C. for ten hours. The melt which was solid on cooling was extracted with boiling water repeatedly. The collected extract was then acidified with a little dilute hydrochloric acid when a very fine black precipitate was obtained. It was allowed to stand overnight and filtered next day. The product thus obtained was further purified by boiling with animal charcoal in alcohol and filtering. The filtrate was diluted with water and evaporated on a water bath till all the alcohol was driven off and the dyestuff was precipitated as before. It dissolves in ethyl and methyl alcohols with a deep mahogany brown colour which deepens in acetone to chocolate-brown and is insoluble in chloroform, benzene and petroleum ether. Addition of alkali produces brownish-violet colour. It is a black powder and does not melt up to 300° C. (Found: C, 61·35%; H, 3·31%. $C_{16}H_{10}O_7$ requires C, 61·14%; H, 3·18%.)

Ortho-cresol-malein.—A mixture of 3 grams of maleic acid and 6 grams of ortho-cresol was heated in an oil bath with a few drops of concentrated sulphuric acid at a temperature of 140–50° C. for 14 hours. The melt on cooling became hard and brittle. It was boiled with water till free from ortho-cresol. The residue was filtered and extracted with dilute alkali and the dyestuff precipitated by gradually acidifying with dilute hydrochloric acid. This was further purified by boiling with alcohol and animal charcoal. The filtrate was diluted with water and alcohol evaporated on water bath, and the dyestuff precipitated from the solution as before, by the addition of a very little quantity of dilute hydrochloric acid. It dissolves in ethyl and methyl alcohols with orange-brown colour and in acetone with chocolate-brown, in chloroform with pale yellow and is insoluble in benzene and petroleum ether. Addition of alkali turns it deep crimson. It is a black powder and melts at 228° C. (Found: C, 77·15%; H, 5·19%. $C_{18}H_{14}O_3$ requires C, 77·69%; H, 5·03%.)

Meta-cresol-malein.—A mixture of 3 grams of maleic acid and 6 grams of meta-cresol was heated with a few drops of concentrated sulphuric acid at a temperature of 125–35° C. for 16 hours. The dyestuff was extracted and purified just in the same way as in the case of ortho-cresol-malein. It dissolves in ethyl and methyl alcohols with yellow brown colour in acetone

chocolate-brown, in chloroform dirty yellow and is insoluble in benzene and petroleum ether. Addition of alkali turns it brown. It is a black powder which melts at 155° C. (Found: C, 77·34%; H, 5·22%. $C_{18}H_{14}O_3$ requires C, 77·69%; H, 5·03%.)

β-Naphthol-malein.—A mixture of 3 grams of maleic acid and 7 grams of β-naphthol was heated in an oil bath at a temperature of 150–55° C. with fused zinc chloride for 10 hours. The brittle melt thus obtained was ground and repeatedly extracted with water in order to get rid of the zinc chloride. The residue was then dissolved in glacial acetic acid, filtered and the dyestuff precipitated from the filtrate by adding water. It was further purified by dissolving in glacial acetic acid and precipitating as before. It dissolves in ethyl alcohol with orange, in methyl with yellow-orange, in acetone with brownish red, in chloroform deep orange and in benzene pale yellow colour, and is insoluble in petroleum ether. It is a dirty brown powder and has got a green fluorescence in solution which gets considerably increased by the addition of alkali and the colour of the solution also becomes bright yellow. On heating it softens at 133° C. and melts at 140° C. (Found: C, 82·71%; H, 4·24%. $C_{24}H_{16}O_4$ requires C, 82·28%; H, 4·00%.)

Meta-amido-phenol-malein.—A mixture of 3 grams of maleic acid and 6 grams of meta-amido-phenol was heated at a temperature of 160–70° C. with a few drops of concentrated sulphuric acid for 6 hours. The melt was then boiled with water and filtered. The residue was then dissolved in dilute alkali, filtered and precipitated by the addition of dilute hydrochloric acid. It was further purified by boiling with alcohol and animal charcoal, filtered and precipitated by diluting and adding a trace of acid. In ethyl and methyl alcohols it dissolves with a dark yellow colour, in acetone yellowish brown and is insoluble in chloroform, benzene and petroleum ether. It is a light brown powder and gives green fluorescence in alcoholic solution. It changes colour at 212° C. and melts at 225° C. (Found: C, 68·14%; H, 4·6%. $C_{16}H_{12}O_3N_2$ requires C, 68·57%; H, 4·28%.)

Resorcinol[5] *and naphthol maleins.*—They were prepared according to the methods already given in literature.

Catechol-succinein.—This was prepared and purified in the same way as the corresponding catechol-malein with the difference that the temperature of the bath was kept at 150–60° C. and the mixture was heated for 12 hours. It is a black powder and dissolves in ethyl and methyl alcohols with dirty greenish yellow, in acetone yellow-brown colour and is insoluble in chloroform, benzene and petroleum ether. Addition of alkali gives dull green colour. It does not melt till 290° C. (Found: C, 68·01%; H, 4·54%. $C_{16}H_{12}O_5$ requires C, 67·60%; H, 4·22 %.)

Pyrogallol-succinein.—This was prepared and purified in the same way as the corresponding pyrogallol-malein with the only difference that the mixture was heated for 14 hours. It is a grey black powder dissolves in ethyl and methyl alcohols with deep mahogany brown and in acetone with a deep chocolate-brown colour and is insoluble in chloroform, benzene and petroleum ether. Addition of alkali turns the solution violet. It shows no signs of melting till 290° C. (Found: C, 60·27%; H, 2·35%. $C_{16}H_{12}O_7$ requires C, 60·75%; H, 3·79%.)

Ortho-cresol-succinein.—This was prepared and purified in the same way as the corresponding ortho-cresol-malein with the difference that the temperature of the oil bath was kept at 150–60° C. for 16 hours. It dissolves in ethyl and methyl alcohols with a chocolate brown colour which deepens in acetone. In chloroform it gives a pale yellow colour and is insoluble in benzene and petroleum ether. Addition of alkali gives reddish violet colour. It is a chocolate brown powder which blackens at 195° C. and melts at 230° C. (Found: C, 77·16%; H, 5·47%. $C_{18}H_{16}O_3$ requires C, 77·14%; H, 5·71%.)

Meta-cresol-succinein.—This was prepared and purified in the same way as the corresponding meta-cresol-malein. The temperature of the oil bath was kept at 145–50° C. It dissolves in ethyl and methyl alcohols and acetone with brownish orange colour, in chloroform with a deep orange and in benzene orange-brown colour and is insoluble in petroleum ether. It is a light brown powder which melts at 112° C. (Found: C, 77·18%; H, 6·06%. $C_{18}H_{16}O_3$ requires C, 77·14%; H, 5·71%.)

α-Naphthol-succinein.—A mixture of 4 grams of succinic acid and 6 grams of α-naphthol was heated with a few drops of concentrated sulphuric acid in an oil bath at a temperature of 140–50° C. for 12 hours. The melt was then boiled with water and filtered. The residue was dissolved in alkali and precipitated by the addition of dilute hydrochloric acid. The product obtained was further purified by boiling with animal charcoal and alcohol and filtered. The alcoholic solution was diluted with water and heated over a water bath till a good deal of alcohol got evaporated. More water was added to the cold solution and dyestuff was precipitated by adding a trace of hydrochloric acid. It is a black powder which dissolves in ethyl alcohol with pink orange colour and green fluorescence, in methyl alcohol with pale pink colour with same fluorescence. In acetone it gives deep crimson, in chloroform chocolate-brown and in benzene brown colour, and is insoluble in petroleum ether. It melts at 185° C. (Found: C, 82·61%; H, 5·02%. $C_{24}H_{18}O_4$ requires C, 81·81%; H, 4·54%.)

Meta-amido-phenol-succinein.—This was prepared and purified in the same way as the corresponding maleic acid compound. It is a violet powder and dissolves in ethyl and methyl alcohols with a violet red and in acetone with a deep violet red colour and is insoluble in chloroform, benzene and petroleum ether. Addition of acetic acid produces deep reddish violet colour. If alkali is added to the alcoholic solution it gives a green fluorescence. It changes colour at 120° C. and melts at 198° C. (Found: C, 67·28%; H, 4·94%. $C_{16}H_{14}O_3N_2$ requires, C, 67·28%; H, 5·01%.)

Resorcinol[6]*-succinein.*—This was prepared according to the method already given in literature.

Meta[7]*-phenylene-diamine malein and succinein.*—These compounds were prepared and purified in the same way as the corresponding cinchomeronein. These were not obtained in sufficient quantity, so they have been studied only qualitatively. They dissolve in ethyl and methyl alcohols with yellow colour and green fluorescence, in acetone orange colour and same fluorescence, and are insoluble in chloroform, benzene and petroleum ether. Addition of acetic acid produces bright yellow colour and the fluorescence is also increased. Malein is dark brown powder which does not melt till 285° C., succinein is clay coloured powder which changes colour at 192° C. and melts at 210° C.

Condensation of resorcinol with mono- and di-bromo-succinic acids.—This was carried out in the same way as in the case of resorcinol-succinein at a temperature of 180–85° C. without any condensing agent. The purification of the dyestuffs was also done in the same way. The product obtained from monobromo-succinic acid was found similar to resorcinol-malein. Dibromo-succinic acid gave substance containing acetylenic linkage which gives a deep green fluorescence in solution which gets intensified by the addition of alkali. It dissolves in ethyl alcohol with crimson colour and in methyl alcohol with deep magenta, in acetone deep crimson, in chloroform orange-red and in benzene orange-brown colour. It is insoluble in petroleum ether. Addition of alkali produces violet crimson colour. It is light mahogany brown powder which darkens at 250° C. and then decomposes. It was not analysed. Its bromoderivative (eosine-like compound) was obtained which is described later on.

Eosine-like compounds.—The bromo compounds of resorcinol-malein and succinein and of the products obtained from mono- and di-bromo-succinic acids with resorcinol, were prepared in the same way as eosine from fluorescein. Bromosuccinyl fluorescein is already known. Bromoresorcinol-malein is a dark red powder which dissolves in ethyl and methyl alcohols

with crimson colour, in acetone with maroon, in chloroform deep orange, in benzene brown and is insoluble in petroleum ether. Addition of alkali produces deep violet crimson colour. It changes colour with decomposition at 185° C. (Found: Br, 52·98%. $C_{16}H_6O_5Br_4$ requires Br, 53·51%.) Bromo compound from resorcinol-acetylenedicarboxylein is a greyish terracotta powder which contracts at 183° C. and melts into globules at 220° C. It dissolves in ethyl alcohol with crimson colour, in methyl alcohol with a deep magenta, in acetone deep crimson, in chloroform orange red, in benzene orange-brown and is insoluble in petroleum ether. Addition of alkali produces violet crimson colour. (Found: Br, 53·03%; $C_{16}H_4O_5Br_4$ requires Br, 53·03%.) Resorcinol-malein prepared from monobromosuccinic acid and resorcinol was also brominated, the eosine-like compound was similar to that obtained from resorcinol-malein. (Found: Br, 52·84%. $C_{16}H_6O_5Br_4$ requires Br, 53·51%.)

TABLE

Absorption Maxima Å (Extinction coefficient 0·9)

Phenols, etc.	Maleins		Succineins	
	In alcohol alone	With alkali	In alcohol alene	With alkali
Phenol	5000	5500	..	5450
Resorcinol	5750	6640	5000	5200
Catechol	5950	6100	4300	4600
Pyrogallol	6800	7000	5970	6750
Ortho-cresol	5400	6300	4800	6250
Meta-cresol	4450	4600	4000	No change
α-Naphthol	5750	5775	4400	4850
β-Naphthol	4750	5250	Not formed	
Meta-amidophenol	4200	No change with acid	5900	5950 with acid
Meta-phenylenediamine	4900	5090 with acid	4450	4750 with acid
Tetra-bromo-resorcinol	6100	6750	6300	No change
Resorcinol-malein from monobromo-succinic acid and resorcinol ..	same as	resorcinol	malein	
Resorcinol-acetylenein from dibromo-succinic acid and resorcinol (1) ..	6450	6950		
Eosine like compound from (1) ..	6800	No change		

We thank Prof. Dr. B. K. Singh for going through the manuscript of the paper.

Summary

(1) Maleic and succinic acids have been condensed with aromatic hydroxy and amino compounds and the properties of the resulting dyestuffs examined. Their study reveals that as expected the dyestuffs obtained from maleic acid were more coloured than the corresponding ones obtained from succinic acid, the only exception being meta-amido-phenol compounds, due obviously to the presence of unsaturation in the chromophore.

(2) The eosine-like bromo compound of resorcinol-malein was also obtained, attempts to prepare which have hitherto been unsuccessful.

(3) Interesting results have been arrived at by the study of bromo-resorcinol-malein in which bromine does not attach itself at the double bond as was originally expected. This has definitely been shown by using brominated succinic acids as starting material and examining the products obtained as well as their bromo derivatives.

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ON CAPILLARY FORCES IN NATURAL SOILS

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Received November 26, 1940

Introduction

It has been well known that when a soil is flooded there is a plane air-water boundary which has a zero pressure deficiency. As water is removed, menisci are formed at the surface and the plane air-water surface is converted into air-water-soil boundary. This stage is marked at the end of the capillary stage and beginning of the funicular stage. Considerable work has been done on the pressure deficiency at this transition stage on materials having uniform size such as " glistening dew ". " Glistening dew " consists of glass beads of uniform size and obtainable in various grades. So far as experiments on this material are concerned, theory and experiment seem to indicate that a soil aggregate might be considered to consist of a bundle of capillary tubes and the pressure deficiency at the transition stage might be represented by the equation $p = KT/2r$. In this equation, p is pressure deficiency, K is capillary coefficient, T is surface tension of the liquid and r is the radius of the particles of soil. While this may be true in the case of ideal, uniform spheres, it is of practical importance to investigate how far conclusions derived from studies of uniform spheres can be applied to natural soil. Again, the method usually employed to determine the pressure deficiency is to place a small column of soil of 3 to 4 cm. in height in a Buckner funnel fitted with a filter-paper and to submit this to a negative pressure. This method precludes the possibility of experimenting with different lengths of columns of soil. The effect of capillarity and negative pressure* on columns of soil which are longer than what is known as the capillary height of soil is of especial importance in irrigation problems. In the experiments to be described in the present paper, the technique has been so arranged that different heights of the column of soil can be examined and the negative pressures determined.

* The term " pressure deficiency " has been used by previous workers for this phenomenon. This differs from the pressure deficiency obtained in porous pot experiments such as those of Roger's. In the experiments now described the negative capillary pressure exerted by the surface of the soil is measured. To avoid confusion, the term " negative pressure " is used in the present paper.

The first series of experiments on negative pressure were carried out on different grades and comparatively short columns of soil, the main purpose here being to examine how far considerations of capillarity can be applied to actual soils. The second series of experiments were conducted with different heights of soils within and above the capillary height. In the third series of experiments, sand was packed in water, the length of the columns being less than the capillary height of the sand. The negative pressure was determined after covering the top of the wet sand with dry sand. The total length of wet and dry sand column was more than the capillary height of sand.

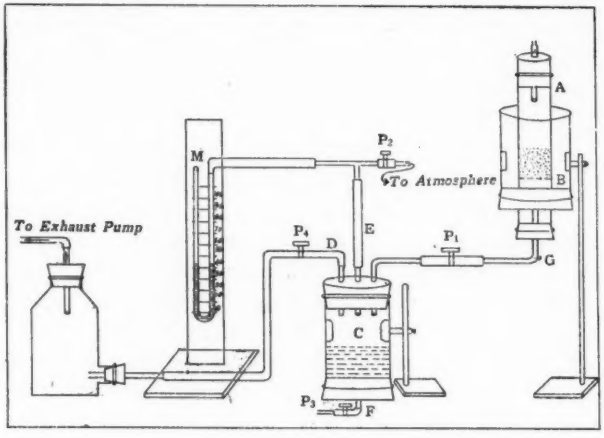

FIG. 1

Arrangement to determine Negative Pressure in Soils

Experimental

The apparatus employed to determine the negative pressure of water in the soil is shown diagrammatically in Fig. 1. It consists of a glass tube AB with a piece of wire-gauze fixed at B. The tube G which comes out of the lower portion of the tube AB passes through a tube in the cork closing the mouth of the tube C. This tube G allows the water of the tube AB to fall into the tube C. The soil to be tested for negative pressure is put in the tube AB above the wire-gauze at B. Any length of the column of the soil can be experimented upon by varying the height of AB. D and E are two tubes connected, as shown in Fig. 1, one to a vacuum pump and the other through a T tube to a mercury or water manometer M. The tube E also enables the tube C to be opened to the atmosphere. Water can be removed from tube C with the help of tube F.

The wider tube surrounding the tube AB had a current of water at a constant temperature of 20° C. flowing through it so as to avoid temperature fluctuations in the soil contained in the tube AB.

The tube AB is first filled with water from below in order that there should be no air in the tube G or in the portion of tube AB below B. The pinch-cock P_1 is then closed and the soil to be tested put into the tube AB. After the soil has been packed in the tube under water, the pinch-cock P_1 is opened and the water begins to drop into tube C from tube G. When the plane water surface reaches the soil surface, the water film in the uppermost layer of the soil exerts a tension and water stops dripping through the end of the tube G. The pressure in C is then decreased till water again starts dripping through the end of the tube G. This takes place when the water film at the surface of soil just breaks. The reading of the manometer M is observed at this point. This gives the negative pressure when the plane water surface at the top of the sand column just breaks.

Results

In the first series of experiments on pressure deficiency, twelve graded samples were investigated. These samples ranged from very coarse sand to very fine silt containing clay.

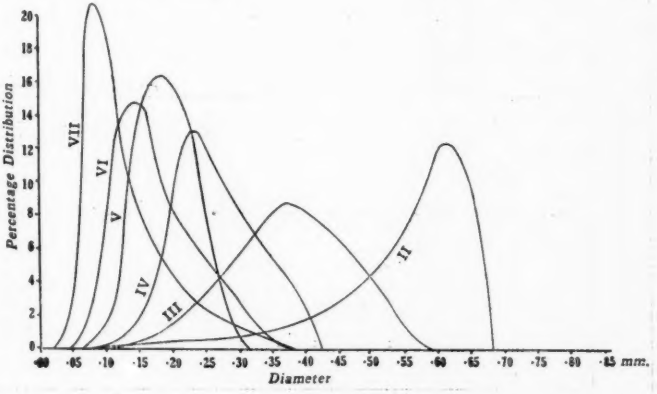

FIG. 2

Size Distribution of Sands

Nos. II to VII

Mechanical analysis of samples.—The mechanical analysis of these samples is shown in Table I and Fig. 2, the analysis of samples 2 to 7 was obtained by the optical lever siltometer[1] and the size distribution curves are given in Fig. 2. Sample No. 1 was analysed with the help of sieves of

TABLE I

Sample No.	Percentage size distribution					Negative pressure in cm. of water	Percentage moisture content	$K = \frac{\rho g h \cdot 2r}{T}$	Statistical mean diameter
	0·50–0·60 mm.	0·60–0·88 mm.	0·88–1·00 mm.	1·00–1·32 mm.	1·32–1·50 mm.				
1	0·24	15·57	29·81	51·84	2·63	11·8	21·5	Could not be calculated	
2		Curve 2 in Fig.				15·2	22·2	11·5	0·545
3		„ 3 „				24·1	23·8	11·89	0·374
4		„ 4 „				36·4	24·7	12·62	0·264
5		„ 5 „				49·2	24·4	12·46	0·191
6		„ 6 „				72·9	25·0	16·50	0·167
7		„ 7 „				86·3	24·4	14·96	0·132
	Below ·002 mm.	·002–·02 mm.	·02–·2 mm.						
8	0·05	4·51	88·72			181·5	24·5	Could not be calculated	
9	9·18	54·85	19·67			200·7	37·7	„	„
10	17·8	58·08	17·65	The remaining contains organic matter		313·9	39·1	„	„
11	1·01	43·59	57·19			391·2	35·5	„	„
12	67·81	19·02	10·10			562·1	47·5	„	„

different mesh sizes, this being too coarse to be analysed by the optical lever siltometer. Samples Nos. 8 to 12 were mechanically analysed by the pipette method, these being too fine to be analysed by the siltometer. Fig. 3 shows the photomicrographs of these samples with a magnification of 1 : 4.

Capillary height of the samples.—The negative pressure of these samples as determined by this apparatus is given in Table I. It shows that the finer the soil the greater the pressure deficiency.

The moisture content of the soil when the water just stops dripping from the end of the tube G was also determined. This is the stage at which the negative pressure was determined. The result is given in Table I.

In the second series of experiments two specimens of sand were examined with different columns to examine the effect of varying the length of the column. The mechanical analysis of the specimens of sands (*a*) and (*b*) are given in Fig. 4. The results are given in Table II.

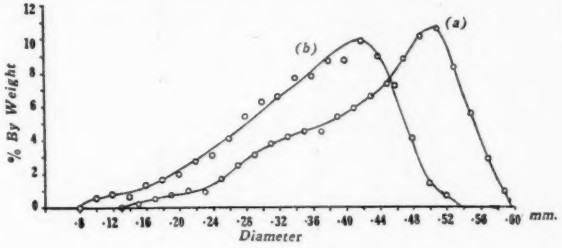

FIG. 4

TABLE II

Height of column	Negative pressure in cm. of water	Height of column	Negative pressure in cm. of water
Sand (*a*)		*Sand* (*b*)	
cm.	cm.	cm.	cm.
5	24	5	32
20	25	20	33
31	23	31	31
50	22	50	30

In the third series of experiments dry sand was introduced on the top of the wet column and the negative pressure was determined after different

intervals of time. The object here was to ascertain the effect of dry sand on the capillary column. The results are given in Table III.

TABLE III

Column of wet sand	Column of dry sand	Time	Negative pressure in cm. of water
		Sand (a)	
cm.	cm.		
20	15	5 mts.	27
20	15	1 hour	26
20	15	2 hours	26
20	15	4 „	26
20	15	24 „	27
20	15	72 „	27
		Sand (b)	
20	15	5 mts.	40
20	15	1 hour	41
20	15	2 hours	40
20	15	4 „	36
20	15	72 „	39

Discussion of Results

The first series of experiments was carried out on samples of sand many of which have been analysed for their particle size by the optical lever siltometer. Their mean diameters have also been worked out and they are given in Table I. The object here was to examine whether the treatment of pore spaces as applied by Slichter can be extended to natural sands.

Slichter[2] treated the pore space in soil particles as a bundle of capillary tubes with an approximately triangular cross-section, assuming the soil particles to be spherical. The mean value of the triangular cross-section was calculated by him as $0{\cdot}2118\ r^2$ where r is the radius of the soil grain, which is spherical and all grains are supposed to be of uniform size. Keen[3] using this idea of the triangular pore space has worked the formula $\rho gh = KT/2r$

where ρgh is called the pressure deficiency. Here ρ is the density of the liquid; g is gravity; h is the height to which the liquid rises; K is the capillary coefficient, T is the surface tension and r is the radius of the grain. This is considered as the fall of pressure in passing from air through the liquid meniscus. Hacket and Stratten called K in the above equation the capillary coefficient. The value of K according to Keen is 19·8. Hackett[4] in experiments on the ascent of oils through sands found that the average value of K was 7·84. Working on glass spheres with benzene as the liquid, he found that the value of K was 9·76. He also calculated the value of K theoretically for a close packing and for cubical packing. The value of K for close packing is 25·86 and for a cubical packing the value of K is 9·66.

Table I gives the values of K determined from the pressure deficiency in the present experiments. If we calculate K for these soils, from their statistical mean value of the diameter m, there is no agreement.

The capillary theory of a bundle of tubes cannot therefore apply to natural soils and any conclusions derived from such a consideration must therefore be wrong. It is certainly true that capillary forces do exist in soil moisture relations, but to consider a natural soil as a bundle of capillary tubes and deduce relations from these is not correct. In the case of natural soils considerations similar to those on uniform spheres do not have a quantitative application.

The second series of experiments indicate that the pressure deficiency is independent of the length of the column, within what is called the capillary height.

The third series of experiments indicate that even if the column of soil is greater than the capillary height, there is no effect on the negative pressure. This is a point of importance to problems of irrigation, because it has been assumed that the presence of dry or wet soil on the top surface brings about considerable changes in the soil moisture relations at or near the water-table. The experiments conducted here show that it does not.

As has been shown in a previous investigation,[5] conditions at the surface do release pressure and cause apparent fluctuations in the water-table, but they do not change the moisture relations of the soil above the water-table. These remain mostly in the original condition, *i.e.*, the presence of the dry soil does not appear to change the moisture gradient near the water-table to any appreciable extent. Experiments conducted by Dr. E. McKenzie Taylor[6] seem also to indicate to similar conclusions. Further investigations are in progress and will be reported subsequently.

We have great pleasure in thanking Dr. E. McKenzie Taylor for his keen interest in the problem.

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PHOTOMICROGRAPHS OF SAMPLES

LINEAR MAGNIFICATION 1: 4

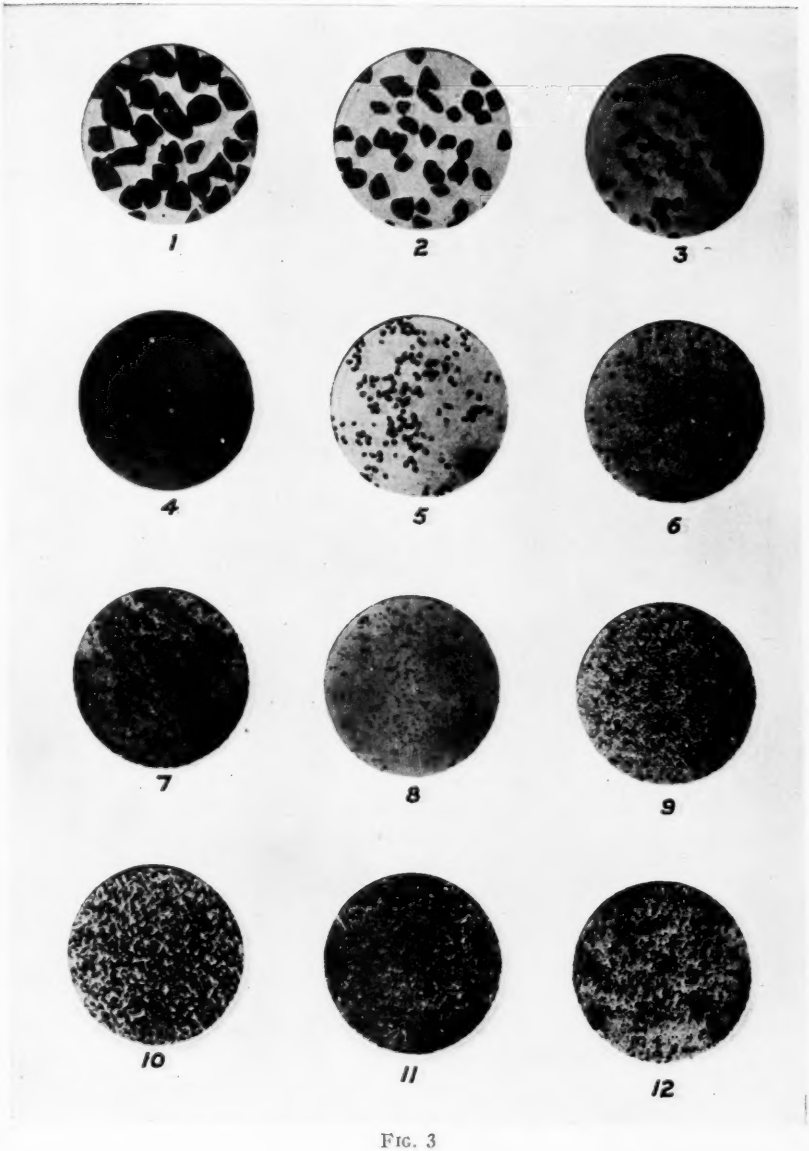

FIG. 3

AN IMPORTANT CONGRUENCE

By Hansraj Gupta

(From the Department of Mathematics, Government College, Hoshiarpur)

Received December 5, 1940

(Communicated by Dr. B. L. Bhatia, D.Sc.)

1. In a letter[1] to Professor G. H. Hardy, Bauer gives a proof based on his identical congruences,[2] of my generalisation[3] of Leudesdorf's Theorem. The object of this note is to give still another proof of the basic result in my paper.

2. In what follows, p denotes a prime $\geqslant 2$. All other small letters denote integers $\geqslant 1$, unless stated otherwise. $S'(m, n)$ denotes the sum of the nth powers of the integers less than m and prime to it. $\mathrm{Pot}_p\, m$ denotes the index of the highest power of p which divides m.

Theorem. For even values of r,

$$S'(p^u, r) \equiv 0 \pmod{p^u} \text{ when } (p-1) \nmid r,$$

$$\equiv 0 \pmod{p^{u-1}} \text{ when } (p-1) \mid r.$$

First, when p is an odd prime.

If $(p-1) \nmid r$, let a be a primitive root of p^u;

then
$$S'(p^u, r) \equiv a^r + a^{2r} + a^{3r} + \cdots + a^{r\phi(p^u)} \pmod{p^u},$$

$$\equiv a^r \{a^{r\phi(p^u)} - 1\}/(a^r - 1) \pmod{p^u},$$

$$\equiv 0 \pmod{p^u};$$

because $\mathrm{Pot}_p \{a^{r\phi(p^u)} - 1\} \geqslant u$, while $\mathrm{Pot}_p (a^r - 1) = 0$.

If $(p-1) \mid r$, and $r = k\, p^\beta (p-1)$ where $(k, p) = 1$ and $\beta \geqslant 0$; let b be a primitive root of $p^{u+\beta+1}$.

Then proceeding as before, we have

$$S'(p^u, r) \equiv b^r \{b^{r\phi(p^u)} - 1\}/(b^r - 1) \pmod{p^u},$$

$$\equiv 0 \pmod{p^{u-1}};$$

because $\mathrm{Pot}_p \{b^{r\phi(p^u)} - 1\} = u + \beta$, while $\mathrm{Pot}_p (b^r - 1) = \beta + 1$.

Now, when $p = 2$, we have

$$S'(2^u, r) = 1^r + 3^r + 5^r + \cdots + (2^u - 1)^r,$$
$$\equiv 2\{1^r + 3^r + 5^r + \cdots + (2^{u-1} - 1)^r\} \pmod{2^u},$$

because r is even.

Since $S'(2, r) \equiv 1 \pmod 2$,

it is easily proved by induction that

$$S'(2^u, r) \equiv 2^{u-1} \pmod{2^u},$$
$$\equiv 0 \pmod{2^{u-1}}.$$

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